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THE POLARIZED ORBITAL APPROXIMATIONS FOR  
ELECTRON IMPACT EXCITATION OF HYDROGEN.

BY

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Thesis submitted to the University of Durham in application for the  
degree of Doctor of Philosophy. 1969.



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## INTRODUCTION.

(1) The purpose of this thesis is to investigate the effects of introducing distortion into the single channel representation of the electron - Hydrogen scattering process. Allowance is made for the indistinguishability of the projectile and atomic electron by means of a symmetry operator.

A brief outline of the contents is as follows:-

Chapter one describes the previous work on elastic cross sections. We start from the early variational approximations in which no distortion is explicitly included. Distortion is introduced by appealing to a form in which interactions satisfy the correct asymptotic behaviour. A fuller formulation is then set down to incorporate all second order interaction terms whose nature is such as to retain the correct asymptotic behaviour. Finally the close coupling approximation provides a form in which all effects may be included implicitly by a complete set expansion of the wave function.

Excitation cross sections are discussed in Chapter 2. Taking the Born approximation as a zero order model, other effects are incorporated e.g. exchange (Born Oppenheimer approximation) and explicit inclusion of the interelectron interaction (Impulse and Vainshtein approximations). Finally the close coupling approximation demonstrates that even in the truncated form presented here very reliable results follow within its range of validity and shall be taken as a standard of comparison in the following work.

Chapter three gives a brief description of the experimental situation to date in both  $1s - 2s$  and  $1s-2p$  scattering. The  $1s-2p$  results are given as perpendicular cross sections. The means by which total cross sections are recalculated is described.

A semi-empirical approximation is described in chapter five. The model, originally due to Drachman, is the adiabatic exchange approximation with the monopole term of the adiabatic polarisation potential partially suppressed, so that the model yields scattering parameters (e.g. the  $e^+ - H$  scattering length) in agreement with experiment. The success of this approximation prompts an investigation of the same technique applied to electron hydrogen scattering. This is considered from the standpoint of the known  $H^-$  bound states. A monopole suppression factor is chosen to provide the best value of the bound state energy.

Chapter four considers in detail the theory used in deriving several polarized single particle projectile wave functions. The evaluation of the polarization and distortion potentials required is given in detail with a description of the characteristics of the potentials. Details are given of the numerical solutions of the polarized single particle function equations. Phase shifts are by a method due to Burgess.

Chapter six uses the single particle wave functions of the previous two chapters to evaluate  $1s-2s$  and  $1s-2p$  cross sections. This end is approached in three stages within the transition matrix, full account being taken of exchange.

- 1) The polarized Born approximation in which distortion is introduced by way of the atomic wave function (the projectile function being a plane wave).

- 2) The single particle polarization approximations in which the single particle function representing the projectile is determined in such a way as to include polarization. This function replaces the plane wave in the symmetrised Born format whilst retaining no explicit polarization in the atomic

wave function.

3) Finally the two effects of polarization are brought together in the full polarization approximation, replacing the symmetrised Born format of the second approximation with the polarized Born format of the first, whilst retaining the distorted single particle functions of the second approximation in place of the plane wave of the first.

## 2. OUTLINE OF THE SCATTERING THEORY REQUIRED.

Whenever the electron hydrogen system is considered in the following work we shall consider an electron (1) incident on a hydrogen atom, comprising a proton as a fixed centre, in the field of which the orbital electron (2) moves. Relative to the fixed centre the electron coordinates are  $\underline{r}_1$  and  $\underline{r}_2$  and the interelectronic distance  $\underline{r}_{12}$  (where  $\underline{r}_1 = (r_1, \theta_1, \phi_1)$  etc.) An alternative set of coordinates describes the position of the centre of mass of the electrons relative to the proton centre  $\underline{R}$ , and the half electronic separation

$$\underline{R} = (\underline{r}_1 + \underline{r}_2) / 2 ; \quad \underline{\rho} = (\underline{r}_1 - \underline{r}_2) / 2 \quad 0.1$$

The coordinates will be identified in figure 0.1. It may be objected that this system regards a finite mass proton as a fixed scattering centre. This criticism may be avoided by transforming to a centre of mass system, the resulting approach being basically equivalent. For electron impact differences will not be significant, except perhaps in threshold problems.

When the projectile-atom separation is large the corresponding interaction potential falls off at least as fast as  $1/r^2$ . In these circumstances the projectile is represented at large distances as an incoming plane wave.

$$F(1) = \exp(i \underline{k} \cdot \underline{r}) \quad 0.2$$

$\underline{k}$  being the projectile momentum. (Units will normally be given in atomic form  $e = \hbar = m = 1$ . An exception will be the energy given in Rydbergs).

The target atomic system is a two body problem whose solution is known



exactly. The Hamiltonian is the sum of the kinetic operator of electron (2) and the coulomb interaction potential  $U(2)$ , between the orbital electron and the proton.

$$H_{02} = -\frac{1}{2} \nabla_2^2 + U(2) ; \quad U(2) = -\frac{1}{r_2} \quad 0.03$$

The corresponding eigen energy  $E_j$ , and the wave function  $\phi_j(2)$ , satisfy the Schrödinger equation, whose solution is a product of a radial function and a spherical harmonic function of the angular coordinate  $\hat{r}_2$  (ref. Schiff - Quantum Mechanics - 1949).

$$H_{02} \phi_j(2) = E_j \phi_j(2) ; \quad \phi_j(2) = R_j(r_2) Y_j(\hat{r}_2) \quad 0.04$$

$\phi_j$  is normalized to unity.

The total energy, the sum of the initial energies of the projectile and the atom, is a constant of time.

$$E = k_i^2 + E_0 \quad (ryd) \quad 0.05$$

As the projectile approaches the atom account must be taken of their mutual interaction potential,

$$V = \frac{1}{r_{12}} - \frac{1}{r_1} . \quad 0.06$$

The resulting three body problem has not been solved exactly. It is the purpose of this thesis to present some approximate solutions to the low energy electron - hydrogen problem. The exact solution can be given formally by the wave function  $\Psi$ , subject to appropriate boundary conditions, satisfying the Schrödinger equation.

$$H \Psi = E \Psi \quad 0.07$$

where the total Hamiltonian  $H$  is the sum of the kinetic operators of the projectile and the atomic Hamiltonian, and the interaction potential  $V$ .

$$H = \frac{1}{2} \nabla_1^2 + H_{02} + V \quad 0.08$$

In the absence of the perturbing potential  $V$  and neglecting rearrangement of the electrons, the system will be in a state  $\psi_j(1,2)$  such that

$$(\frac{1}{2} \nabla_1^2 + H_{02} - E_j) \psi_j = 0 \quad 0.09$$

and hence

$$\psi_i(1, 2) = \psi_j(2) F(1) \quad C.10$$

The theory of scattering has been treated in many books (e.g. Goldberger and Watson - 1964). It will suffice here to sketch the theory and quote the results essential to this thesis.

Consider eq. 7 at an energy  $W = E + i\epsilon$ . That is

$$(H - W) \underline{\Psi}_i^{(\epsilon)} = 0 \quad \text{OR} \quad (H_0 - W) \underline{\Psi}_i^{(\epsilon)} = -V \underline{\Psi}_i^{(\epsilon)} \quad C.11$$

Since  $(H - W)$  is never null on the space of  $H_0$ , a particular integral is

$$\underline{\Psi}_i^{(\epsilon)} = -1/(H_0 - W) \cdot V \underline{\Psi}_i^{(\epsilon)} = (E - H_0 + i\epsilon)^{-1} V \underline{\Psi}_i^{(\epsilon)} \quad C.12$$

The formal solution may then be written as

$$\underline{\Psi}_i^{(\epsilon)} = \psi_i + (E - H_0 + i\epsilon)^{-1} V \underline{\Psi}_i^{(\epsilon)} \quad C.13$$

Detailed study shows that  $(E - H_0 + i\epsilon)^{-1}$  is a representation of the Greens function of the unperturbed problem, say  $G_0^+$ , so that we can write in the limit  $\epsilon \rightarrow +0$ ,

$$\underline{\Psi}_i = \psi_i + G_0^+ V \underline{\Psi}_i \quad C.14$$

Rearranging this expression we conclude that the outgoing spherical wave solution of e.g. 7 provides

$$\underline{\Psi}_i = \psi_i + G^+ V \psi_i \quad C.15$$

where  $G^+$  is the Greens function operator of the total Hamiltonian formally written as

$$G^+ = (E - H + i\epsilon)^{-1} \quad C.16$$

Defining the T-matrix corresponding to the process  $i \rightarrow f$  to be

$$T = \langle \psi_f | V | \underline{\Psi}_i^+ \rangle \quad C.17$$

and assuming the asymptotic form

$$\underline{\Psi}_i^+ \sim (e^{i\mathbf{k}_i \cdot \mathbf{r}} + f(\theta_i) e^{i\mathbf{k}_f \cdot \mathbf{r}}) \quad C.18$$

where the differential cross section  $I(\theta)$ , is

$$I(\theta) = |f(\theta_i)|^2 \quad C.19$$

the properties of the Greens function operator give

$$f(\theta) = \frac{1}{2\pi} T_{if} \quad \text{C.20}$$

The total cross section in which all particles are distinguishable follows

$$Q(i \rightarrow f) = k_f / k_i \int |T_{if}|^2 d\Omega \quad (\text{units of } a_0^2) \quad \text{C.21}$$

Integration is over the angular space  $\hat{k}_f$  of the final momentum of the projectile. An alternative approach to cross sections, can be found in terms of the momentum transfer  $p$ .

$$Q(i \rightarrow f) = \frac{1}{k_i^2} \int_{p_{\min}^2}^{p_{\max}^2} |T_{if}|^2 d(p^2) \quad (\text{units of } \pi a_0^2) \quad \text{C.22}$$

The momentum transfer and limits of integration are related to the initial and final momentum,  $k_i$  and  $k_f$ , and the energy change  $\Delta E$  by

$$p = k_i - k_f; \quad p_{\max} = |k_i| + |k_f|; \quad p_{\min} = ||k_i| - |k_f||; \quad \Delta E = k_i^2 - k_f^2 \quad \text{C.23}$$

For problems in which particles are indistinguishable the Pauli principle requires that the total wave function should be antisymmetric in the interchange of these particles. For electron scattering on hydrogen atoms, cross sections depend on the relative spin orientations of the electrons. These have different probability weighting factors for singlet (+ve, spin antiparallel) and triplet (-ve, spin parallel) orientations. The corresponding cross sections are related to the spin averaged cross section by

$$Q = \frac{1}{4} [Q^+ + 3Q^-] \quad \text{C.24}$$

In some cases a partial wave expansion of  $\Psi_i$  is useful. The asymptotic form of the partial wave function may be expressed in a number of ways. The reactance matrix notation is concerned with real wave functions. The matrix  $R$  is defined by its elements  $R_{ij}$  connecting the  $i$ th and the  $j$ th channel. In particular if only channels  $i$  and  $j$  are open

$$\Psi_j^+ \sim_{r \rightarrow \infty} A_{ij} [\sin(k_j r - l_j \pi/2) + R_{ij} \cos(k_j r - l_j \pi/2)] \quad \text{C.25}$$

$i$  being associated with the initial state of the system. In the single channel (elastic scattering) process  $R$  relates simply to the phase shift  $\eta$

$$R = \tan \eta \quad \text{C.26}$$

An alternative formulation defines cross sections through the scattering matrix S, by the asymptotic form

$$\Psi_i^+ \underset{r \rightarrow \infty}{\sim} A_{ij} [e^{-i(k_j r - l_j \pi/2)} + S_{ij} e^{i(k_j r - l_j \pi/2)}] \quad C.27$$

The R and S matrices are related to the T- matrix by

$$T = -2iR / (1 - iR) \quad ; \quad S = (1 - R) / (1 + R) \quad C.28$$

The choice of asymptotic form relates to their different properties.

The R - matrix is analytically continuable at thresholds to higher channels.

The S- matrix deals directly with bound states (poles in the S- matrix) and resonances (zeros of the S- matrix).

### VARIATIONAL PRINCIPLES.

Subject to certain restrictions variational principles provide bounds on physical quantities, such as scattering lengths. Thus many methods of low energy scattering can be related within the variational form of the Schroedinger equation.

$$\delta I = 0 \quad C.30$$

where

$$I = \int \Psi_i (H - E) \Psi_i d\tau \quad C.31$$

subject to arbitrary variations of  $\Psi_i$ , satisfying the same boundary conditions as the exact solution. This has the advantage that if  $\Psi_i$  is a trial function satisfying the above conditions then it meets with the exact function in giving  $I$  ( $= 0$ ) exactly, up to second order in the error in the wave function.

Since the Hamiltonian is diagonal in the total orbital and spin angular momenta, L and S, and their associated projections,  $M_L$  and  $M_S$ , we can consider variations of individual terms of I in which these quantities are conserved. Introducing the diagonalised form of the wave function corresponding to the jth exit channel

$$\Psi_{j, L M_L, M_S} = \chi_j(\underline{r}, \hat{r}) u_{ij}(r) \quad C.32$$

we note that

$$I_{LS m_L m_S} \equiv \int \eta_i (H - E) \Psi_{i, LS m_L m_S} d\tau = 0 \quad 0.33$$

This follows since  $\Psi_{\text{exact}}$  satisfies the Schroedinger equation.

Consider small variations of the type

$$\begin{aligned} \delta \Psi &= \Psi_* - \Psi_{\text{exact}} = \eta_j \delta u_{ij}(r_i) \\ &\sim \eta_j A_{ij} \cos(k_j r_i - \frac{1}{2}\pi) \delta R_{ij} / (k_j r_i) \end{aligned} \quad 0.34$$

Then first variations of I gives

$$\delta I = \int \Psi (H - E) \delta \Psi d\tau + \int \delta \Psi (H - E) \Psi d\tau \quad 0.35$$

Applying Greens' theorem to the one dimensional case of the first integral, provides

$$\delta I = -\frac{1}{2} \int ds \left\{ u(r_i) \frac{d}{dn} \delta u(r_i) - \delta u(r_i) \frac{d}{dn} u(r_i) \right\} + \int \delta \Psi (H - E) \delta \Psi \quad 0.36$$

where n is normal to the surface  $\hat{s} = \mathbf{r}^i d\mathbf{f}$ . Ignoring terms of order  $(\delta \Psi)^2$

we find that small variations of the quantity  $(I - A^2 R / 2k)$  are zero.

This provides the basis of the variational principle which allows any elastic or reaction cross section to be calculated. It follows that a correction to R can be obtained with the Kohn variational principle (1948).

$$Rk = R - 2k I^2 / A^2 + 0 (\delta \Psi^2) \quad 0.37$$

The alternative Hulthen form (1948) demands that it be zero.

The problem remains to give some consideration to the residual error term

$$E_r = \int \delta \Psi (H - E) \delta \Psi d\tau \quad 0.38$$

Rosenberg, Spruch and O'Malley (1960) have extended error estimations originally proposed by Kato (1951) to include compound systems. For  $k = 0$  and no bound states of the system, they have shown that the Kohn variational principle provides an upper bound. For bound state inclusive cases the error term will not be guaranteed less than zero, the requirement providing an upper bound, unless  $\delta \Psi$  is orthogonal to the exact bound state wave functions. Since the latter is orthogonal to the exact scattering

wave function, the Hulthen - Kohn variational principles give an upper bound on the scattering length if the trial wave function is chosen to be orthogonal to the bound state wave function.

## CHAPTER 1.

### (1) Methods of Elastic Scattering

Different variational and quasi-variational methods can be classified according to assumptions made regarding the structure of  $\bar{\Psi}_i^+(1,2)$ , eq. 0.31.

The simplest such method assumes that

$$\bar{\Psi}_i^+(1,2) = F(1) \phi_0(2) \quad 1.1$$

where  $\phi_0(2)$  is the known ground state atomic wave function. Note that this form is unsymmetrised and therefore makes no distinction between singlet and triplet scattering. Variation with respect to  $F(1)$  yields as its Euler - Lagrange equation the Schroedinger equation for the projectile in an averaged central field of the unperturbed atom. It is referred to as the central field approximation. Using an expansion in terms of spherical harmonic functions and corresponding reduced radial functions.

$$F(1) = \sum_l u_l(r_1)/r_1 \cdot Y_{l0}(\hat{r}_1) \quad 1.2$$

the variational expression yields a set of second order differential equations.

$$D_u U_l = \left[ \frac{d^2}{dr_1^2} - l(l+1)/r_1^2 + k^2 + 2V_c(1) \right] u_l(r_1) = 0 \quad 1.3$$

$$\text{where } V_c \equiv \bar{V} = \int \phi_0(2) V \phi_0(2) dr_2$$

A solution is found satisfying a condition of finiteness at the origin, usually that  $U_l(0) = 0$  and  $U_l'(0) = 0$ .

Phase shifts are evaluated (table 1.1) by comparing the asymptotic form of the solution with eq. 0.25. Morse and Allis introduced the exchange form with the wave function.

$$\bar{\Psi}(1,2) = F(1) \phi_0(2) \pm F(2) \phi_0(1) \quad 1.4$$

It is exactly equivalent to an analytic continuation in  $k^2$  of the usual restricted Hartree - Fock equations for the two electron problem. Note that it does not give binding for  $H^-$ . The Euler - Lagrange equation is

TABLE 1.1

S-wave phase shifts.

<u>Singlet</u>	(1)	(2)	(3)	(4)	(5)	(6)	(7)
$k(a.u)$							
0.00	RSO=6.23	8.10	6.50	5.80	7.42	6.74	
0.00		3.06	3.08	3.08	3.07	2.49	
0.05		2.75	2.82	2.86	2.77	1.87	
0.10	0.72	2.40	2.52	2.58	2.44	1.54	2.55
0.20	0.97	1.87	2.03	2.11	1.91	1.20	2.07
0.30	1.05	1.51	1.65	1.75	1.54	1.01	1.70
0.40	1.06	1.24	1.37	1.47	1.26	0.88	1.41
0.50	1.04	1.03	1.16	1.25	1.04	0.81	1.20
0.75		0.69	0.82	0.91	0.69		
1.0	0.90	0.54	0.67	0.76	0.53		

Triplet.

$k$

0.00	RSO=1.91	2.35	1.90	1.90	1.68	1.89	
0.01		3.12	3.12	3.12	3.12	2.93	
0.05		3.02	3.05	3.05	3.05	2.66	
0.10		2.91	2.95	2.95	2.95	2.46	2.94
0.20		2.68	2.74	2.73	2.73	2.19	2.71
0.30		2.46	2.53	2.52	2.52	2.01	2.50
0.40		2.26	2.33	2.32	2.33	1.87	2.29
0.50		2.07	2.15	2.13	2.15	1.76	2.10
0.75		1.68	1.76	1.74	1.77		
1.00		1.39	1.48	1.46	1.49		

Continued.....



TABLE 1.1 (Cont'd.)

RSO = Rosenberg et al (1960) - upper bound on scattering length

For  $k = 0$ , results are scattering lengths. The choice of positive sign follows the convention of Temkin and Lamkin (1960).

- 1) Central Field approximation (unsymmetrised) - (present calculation).
- 2) Central Field approximation (symmetrised) - one state approximation  
(present calculation).
- 3) Exchange Adiabatic approximation - Temkin and Lamkin (1960).
- 4) Polarized Orbital approximation - Temkin and Lamkin (1960).
- 5) Extended Polarization approximation - Callaway et al (1968).
- 6) Close Coupling approximation - (1s-2s-2p state) - Burke and Schey (1962)
- 7) Schwartz variational approximation (1961).

TABLE 1.2.

States included.	1s	1s-2s	1s-2p	1s-2s-2p	1s-2s-2p- 3s-3p	Schwartz
Energy = 0.55	.700	.735	.735	.785	.798	.908
Energy = 0.60	.670	.712	.704	.771	.782	.894

integro differential in nature and has been solved numerically (table 1.1).

An improvement on the exchange approximation follows with the use of a trial wave function of non-separable form, for example,

$$\Psi^{\pm}(1,2) = \phi_0(2)F(1) \pm \phi_0(1)F(2) + \underline{\Psi}^{\pm}(1,2) \quad 1.5$$

The asymptotic form of the correlation function is required to vanish at least as fast as  $r_1 \underline{\Psi}^{\pm}(1,2) \rightarrow 0$  as  $r_1 \rightarrow \infty$ . Castillejo et al (1960) have shown that the correct asymptotic form of the interaction potential has an inverse fourth power behaviour,  $\propto /r_1^4$ , the constant being the polarizability. To account for the adiabatic distortion of the atom by the projectile, a potential term representing the interaction between the projectile and the induced dipole has been added to the Euler-Lagrange equations of the central field exchange approximation by Bates and Massey (1947). The interaction term is chosen as  $\alpha/(r_1^2 + d^2)$ , where  $\alpha$  is the known atomic polarizability and  $d$  is a suitably chosen cut off parameter preventing divergence at the origin. This is the exchange adiabatic approximation in its simplest form. Whilst this gives explicit allowance for long-range polarization effects, it is essentially empirical and cannot be obtained by a consistent variational argument. The asymptotic form of the equations satisfied by the  $l$ th partial wave give

$$\left[ \frac{d^2}{dr_1^2} - l(l+1)/r_1^2 + \alpha/r_1^4 + k^2 \right] u_l(r_1) = 0 \quad 1.6$$

This is shown by Bransden (1958) to give phase shifts which vary as  $k^2$  for small  $k$ , and  $l$  greater than zero, which is in agreement with the requirement of general potential theory (Newton 1961).

## (2) Method of Polarised Orbitals

Rather than make ad-hoc additions to the one particle Euler Lagrange equations Temkin (1959), and Temkin and Lamkin (1960), introduced the adiabatic distortion by modifying the Ansatz for the wave function. A

function  $\bar{\Phi}_{\text{pol}}(1,2)$  of coordinates of both electrons is chosen, so that when added to  $\Phi(2)$  in eq. 4 it provides the correct asymptotic form (eq. 6), for large separations.

First order perturbation theory gives the wave function for an atom interacting via a potential  $V(1,2)$  as

$$\Psi(1,2) = \Phi_0(2) + \mathcal{D}^{(1)}(1,2) \quad 1.10$$

$$\text{where } \mathcal{D}^{(1)}(1,2) = - \sum_{\alpha} \langle \alpha | V | 0 \rangle \Phi_{\alpha}(2) / (\bar{E}_{\alpha} - \bar{E}_0) \quad 1.11$$

the sum being over all state  $\alpha = (n \ l \ m)$ , except  $\alpha = 0$ . This may be rewritten in a form consistent with our interest in the asymptotic region ( $r_1 > r_2$ )

$$\mathcal{D}^{(1)}(1,2) = - \sum_{l=1}^{\infty} \frac{2}{r_1^{l+1}} P_l(\cos \theta_{12}) / (4\pi)^{1/2} \frac{\sum_{n,l} \langle n,l | r^{-1} | 0 \rangle}{(\bar{E}_n - \bar{E}_0)} R_{nl}(r_2) \quad 1.12$$

Though this cannot be written in closed analytic form the formal expansion above can be evaluated using the first order perturbation equation

$$[-\nabla_1^2 - 2/r_1 - \bar{E}_0] \mathcal{D}^{(1)}(1,2) = 2 \int d\mathbf{r}_2 \frac{r_2^l}{r_1^{l+1}} \Phi_0(2) P_l(\cos \theta_{12}). \quad 1.13$$

This suggests the expansion

$$\mathcal{D}^{(1)}(1,2) = \sum_{l=1}^{\infty} \mu_{l \rightarrow 1}(r_1)/r_1 P_l(\cos \theta_{12}) / (4\pi)^{1/2} / r_1^{l+1}. \quad 1.14$$

The radial functions are found to obey equations of the Sternheimer type (1954) and for bound states are of the form

$$\mu_{l \rightarrow 1}(r_1) = 2 \exp(-r_1) [r_1^{l+2}/(l+1) + r_1^{l+1}/l]. \quad 1.15$$

Use of eq.12 implies that this form of the solution is only meaningful outside the atom. The inner region is avoided by means of a step function  $\epsilon(1,2)$ .

$$\epsilon(r_1 > r_2) = 0 \quad \epsilon(r_1 > r_2) = 1 \quad 1.17$$

Keeping only the dipole term of the expansion, eq. 14 reduces to

$$\bar{\Phi}_{\text{pol}}(1,2) = \Phi_0(2) - \epsilon(1,2)/r_1 e^{-r_1}(r_1^2 + 2r_1) P_1(\cos \theta_{12}) / (4\pi)^{1/2}. \quad 1.18$$

By choosing a trial function

$$\bar{\Psi} = (1 \pm P_{12}) \bar{\Phi}_{\text{pol}}(1,2) F(1) \quad 1.19$$

and projecting the Schrodinger equation onto the unperturbed atomic wave function Temkin obtained an equation for the  $l$ th partial wave of  $F(1)$

$$De \mu_l(r) \pm r R_{1s}(r) F_l(r) = \alpha(r)/r^4 \mu_l(r) \pm \mu_{l \pm 2}(r) G_l(r) \pm \frac{2}{3} r R_{1s}(r) \int_0^\infty \frac{R_{1s}(r_2) \mu_l(r_2) dr_2}{r_2^2} \delta_{ll}$$

where

(1.20a)

$$\alpha(r) = 9/2 - e^{-2r} (r^5 + 9r^4/2 + 9r^3 + 27r^2/2 + 27/2 r + 27/4)$$

(1.20b)

$$G_l(r) = -\frac{2}{3} (1+k^2) \delta_{ll} \int_0^\infty \frac{R_{1s}(r)}{r} \mu_l(r) dr + \frac{4l}{(2l+1)(2l-1)} \int_0^\infty \frac{R_{1s}(r)}{r^{l+2}} \mu_l(r) dr + 4(1+l) r^{l+1} \int_0^\infty \frac{R_{1s}(r)}{r^{l+4}} \mu_l(r) dr$$

(1.20c)

$$F_l(r) = -(1+k^2) \delta_{l0} \int_0^\infty r R_{1s}(r) \mu_l(r) dr + 2/(2l+1) \int_0^\infty r R_{1s}(r) \delta_l(1,2) \mu_l(r) dr$$

$D_l$  is defined as the central field operator (eq. 1.3) and  $\delta_l(1,2)$  is the

$l$ th partial term in an expansion of  $V$ . Polarization terms are arranged on the right hand side of the equation. Dropping the last two terms on the right hand side of (1.20a) gives the exchange adiabatic approximation.

Comparison of s-wave singlet phase shifts (table 1.1) indicates that the polarized orbital results are in much better agreement with the essentially correct Schwartz (1961) results than were those of the exchange approximation. For triplet phase shifts the exchange approximation results are of comparable merit with those of the two polarization approximations; the discrepancy is small.

The results can be understood as follows. The method of polarized orbitals takes account of long range distortion, but not short range correlation effects. For triplet scattering the Pauli principle acts to keep the two electrons apart. Correlation is less important and better results might be expected than for singlet scattering.

That this is not the case suggests that the method overestimates, polarization at small separations whilst in the singlet case too much polarization is compensated for by too little correlation.

The low energy behaviour may be investigated by comparison of scattering lengths with the upper bound set by Rosenberg et al (1960 (3)). The fact

that the singlet s-wave exchange adiabatic results exceed the bound, while the full polarized results lie below indicates that the exchange polarization terms are meaningful.

Sloan (1964) has rederived Temkin's formulation showing that for p-wave scattering eq. 20 should be modified on the right hand side by

$$H(\mathbf{r}) \pm \frac{4}{3} \delta_{\mathbf{r}} e^{-2r} \left[ \left( \frac{3}{2} r^2 + \frac{1}{2} r - 3 \right) u_1(r) - \left( \frac{1}{2} r^2 + r \right) \frac{d}{dr} u_1(r) \right]. \quad 1.21$$

These terms arise from the action of the Laplacian operator  $\nabla^2$  on the step function  $\epsilon(1,2)$ . Their significance may be questioned on the grounds that the step function produces an unphysical discontinuity in the wave function. However, if the step function is replaced by a smoothly varying cut off function the extra terms which arise tend to zero as the function approaches the step function. Furthermore the property of the variational principle is lost if the extra terms are ignored.

The modified eq. 20 has been employed by Sloan to recalculate p-wave polarized orbital phase shifts (see fig. 1.1). For the singlet case these are smaller than the unmodified results and closer to the exchange approximation values than were the Temkin and Lankin values. Triplet results are somewhat increased with the modified equation leading to larger total elastic cross sections. The singlet p-wave contribution to cross sections is small. The experience of Sloan's  $\text{He}^+$  triplet phase shift calculation indicates a value lying between the modified and unmodified polarized orbital values. Such being the case the corresponding p-wave exchange adiabatic results are too large.

In  $e^- - \text{H}$  total elastic cross sections the s-wave is very much dominant. Nonetheless the modified version does move the cross sections slightly towards those of the extended polarization approximation of Callaway et al (1968), for the higher energy range (see fig. 1.4).

In an attempt to retain the better features of Temkin's polarized orbital method whilst avoiding some of the drawbacks Labahn and Callaway suggested a more complete formulation. The general philosophy behind their approach lies both in the choice of a variational principle and in the preference of a full perturbation treatment of the adiabatic potential of the electron Helium atom scattering problem. The strong similarity of the approach to that used in the electron-hydrogen problem is apparent from the choice of a truncated perturbation equation and the choice of hydrogen type wave functions as the basis of second order interaction terms.

The hydrogen atom is basically simple and is the only system for which exact solutions are known for both unperturbed and first order perturbed equations. Nonetheless there are certain advantages to working with the helium atom. As the ground state wave function must satisfy the Pauli principle the helium ground state is a singlet spin state. Consequently, the total wave function is a doublet, whereas both singlet and triplet states determine cross sections in electron-hydrogen scattering. Further the presence of the second electron in the helium atom tends to shield the interaction effects of the scattering electron. The resulting polarization is not as great as in the hydrogen atom problem. However since the correlation is now between an external electron and a closed shell, rather than between an external electron and an open shell as in the  $e^- - H$  problem correlation is expected to be relatively less important than is polarization. Finally the chemical inertness of the helium atom makes for an easier experimental medium providing more reliable results.

The wave function of the electron-helium system is chosen to incorporate both symmetry and distortion effects.

$$\Psi(1, 2, 3) = 1/\sqrt{3} \{ \psi^{(1)}(1, 2)\phi(3) + \psi^{(1)}(2, 3)\phi(1) + \psi^{(1)}(3, 1)\phi(2) \}$$

1.30

where  $\phi(3)$  describes the projectile motion and  $\psi^{(n)}(i, j)$  are bound state

wave functions determined to first order in perturbation. Thus

$$\psi^{(n)}(i, j) = \psi_0(i) \psi_0(j) + \psi_0(i) \chi(j, n) + \psi_0(j) \chi(i, n) \quad 1.31$$

where  $\psi_0$  is the unperturbed Hartree Fock wave function and  $\chi$  its first order correction due to interaction with the projectile.

The variational principle is restricted to variation of the unknown projectile wave function  $\phi(n)$ . Projecting the Schroedinger equation onto the distorted atomic wave function gives

$$\int \psi^{(n)}(1, 2) \{H - E\} \{ \psi^{(n)}(1, 2) \phi(3) - \psi^{(n)}(3, 1) \phi(2) \} d\underline{r}_1 d\underline{r}_2 = 0 \quad 1.32$$

where H is the Hamiltonian of the three electron system and E is the total energy. The resulting equations are complicated and can be approached through a series of approximations.

The adiabatic exchange approximation of Labahn and Callaway (1964) is obtained by neglecting the first order perturbed orbital in all terms but one direct interaction contribution, giving

$$\int \psi_0^*(1) \psi_0^*(2) \{H - E\} \{ \psi^{(n)}(1, 2) \phi(3) - \psi_0(1) \psi_0(3) \phi(2) \} d\underline{r}_1 d\underline{r}_2 = 0 \quad 1.33$$

In line with the exchange adiabatic approximation of Temkin only the dipole part of the resulting polarization potential is kept.

The more inclusive dynamic exchange approximation (Labahn and Callaway, 1966) retains all direct terms of eq.30 whilst neglecting exchange terms depending on the first order perturbed orbital, giving

$$\int \psi^{(n)}(1, 2) \{H - E\} \psi^{(n)}(1, 2) d\underline{r}_1 d\underline{r}_2 \phi(3) - \int \psi_0^*(1) \psi_0^*(2) \{H - E\} \psi_0(1) \phi(2) d\underline{r}_1 d\underline{r}_2 \psi_0(3) = 0 \quad 1.34$$

Neglect of exchange polarization terms ignores some first order terms whilst the second order direct polarization potential is retained. Rather than solve the Hartree Fock perturbation equations to determine these higher order potentials use is made of the Bethe (1943) polarization potential based on an exponential variational function. Callaway (1957) and Chang

and McDowell (1968) have shown that for a  $(1s)^2$  pair the Bethe dipole polarization potential is an extremely accurate representation of the full H.F. polarization potential, provided the H.F. value of the polarizability is used. It follows that at small  $r$  the potential has the  $r^2$  behaviour of Bethe's potential rather than the  $r$  behaviour of Temkin's model.

It remains to extend the dynamic exchange approximation to include the neglected higher order exchange terms of eq. 30. To this end Callaway et al (1968) reformulated the problem in a more rigorous projection operator approach whilst keeping in mind the considerations of their previous work. However, difficulties arising from the choice of a projection operator for systems with identical particles, formally restricted considerations to distinguishable particles. Neglecting higher order exchange interactions the extension to identical particle scattering is straight forward. The resulting extended polarization approximation and the dynamic exchange approximation are related within the form of the second order integro-differential equation

$$\begin{aligned} [-\nabla^2 - \epsilon/r_3 + 2V_c(z) + 2V_{pol}(z) - 2D(z) - k^2] \phi(z) = \\ = [(\epsilon - k^2) \int \psi_0^*(z) \phi(z) dz_1 + 2 \int \psi_0^*(z)/r_{21} \cdot \phi(z) dz_2] \psi_0(z) \end{aligned} \quad 1.35$$

where  $V_c$  is the H.F. interaction potential and  $V_{pol}$  the polarization potential formally identical with the previous definitions.

Essentially the outcome of the projection operator formalism is not different than that of the dynamic exchange approximation. Such differences as do apply arise from the different definitions of the first order perturbed orbital  $\chi$ , and its effect on the kinetic operator  $\nabla^2$  to produce the potential operator  $D$ . In line with the usual practice in perturbation theory the choice of the dynamic exchange approximation was to orthogonalise the first order perturbed orbital with respect to the unperturbed  $\psi_0$ . This property provides

$$D(z) \phi(z) = \int \chi^*(z, 3) \{ [\nabla_3^2 \chi(z, 3)] + 2 [\nabla_3 \chi(z, 3)] \cdot \nabla_3 \} dz_1 \phi(z) \quad 1.36$$



The second term may be interpreted physically as a correction to the adiabatic theory to account for the delay in the redistribution of the atomic wave function following the motion of the projectile. The projection operator formalism demands the full distorted atomic wave function be normalised to unity. Keeping terms up to first order this requires

$$\int \{ \psi_0^*(2) \chi^*(2,3) + \chi^*(2,3) \psi_0(2) \} d\underline{r}_2 = - \int | \chi(2,3) |^2 d\underline{r}_2 \quad 1.37$$

This gives rise to the alternative distortion potential

$$D(3) \phi(3) = - \int | \nabla_3 \chi(2,3) |^2 d\underline{r}_2 \quad 1.38$$

Through its neglect of the correct normalisation condition the dynamic exchange approximation will be inadequate in the formal sense. Nevertheless theoretical considerations indicate that phase shift differences against the correct extended polarization phase shifts will be small for electron helium scattering. This may be seen as follows. Define a new projectile wave function  $\phi'$  such that

$$\phi(3) = \phi'(3) \exp \left[ - \int | \chi(2,3) |^2 d\underline{r}_2 \right] \quad 1.39$$

Since for large separations  $R$ , the integrand  $| \chi |^2$  is proportional to  $R^{-4}$  the same phase shifts will be obtained from  $\phi$  and  $\phi'$  to within the error due to other neglected terms. Substituting  $\phi$  into eq.32 gives  $\phi'$  satisfying a form not dissimilar to the projection operator form of eq.35. The difference is a fourth order term,  $|\int \chi(2,3) \nabla_3 \chi(2,3) d\underline{r}_2|^2$  and modified exchange terms. Explicit calculations for electron helium scattering suggests that these are small. Distortion potentials have been constructed by Drachman (1965) in numerical form. Callaway et al have produced an analytic expansion of the potential, corresponding to an expansion of in terms of Legendre polynomials.

Eq.32 and 35 have been solved for electron-helium scattering to provide phase shifts, from which total cross sections were calculated. In fig 1.4

comparison is made between the experimental results of Golden and Bandel (1965) and several theoretical approximations: 1) Adiabatic Exchange Dipole (retaining only the dipole component of the polarization potential). 2) Adiabatic Exchange Total (retaining all the significant polarization potential contributions). 3) Extended Polarization. The dynamic Exchange values of Labahn and Callaway (1966) coincide almost exactly with the experimental values above 5 eV. Corresponding scattering lengths are

$$Q_{GB} = 1.15, \quad Q_{EP} = 1.151, \quad Q_{AED} = 1.132, \quad Q_{AET} = 1.097, \quad Q_{DE} = 1.186$$

Theoretical momentum transfer cross sections are given in fig 1.3 in comparison with the experimental values of Crompton et al (ref. Callaway et al (1968)). The Dynamic Exchange values lie between the E.P. and the theoretical values differing by up to 6%.

For electron-hydrogen scattering Callaway et al (1968) have calculated two sets of results. One uses the three component ( $l = 0, 1, 2$ ) expansion for the polarization potential while the other uses an exact form due to Dalgarno and Lynn (1957). The distortion potentials are not known in closed form. Instead they use the monopole and dipole components only. The resulting phase shifts were essentially identical except at very low energies and only those values from the three component polarization potential will be considered here.

The extended polarization s-wave phase shifts can be compared with the two polarization approximations of Temkin and Lamkin and the variational values of Schwartz (1961). (see table 1.1)

Triplet s-wave phase shifts show good agreement between all the approximations. This being the dominant contribution to elastic cross

sections, especially at high energies, accounts for the closeness in this process of the EP values with those of Sloan's modified polarized orbital approximation above  $k^2 = 0.09$  au. (fig 1.5)

The singlet E.P. values show best agreement with the exchange approximation, which making no allowance for polarization would seem to confirm the assertion of an excessive allowance for polarization effects by the polarized orbital approximation of Temkin and Lamkin.

Scattering lengths for the E.P. approximation (table 1.1) are seen to exceed the bound of Rosenberg et al (1960). Corresponding singlet and triplet values provided by the E.P. approximation with the full Dalgaard and Lynn polarization <sup>potential</sup> ( $a_+ = 7.26$ ,  $a_- = 1.68$ ) differ insufficiently from the partial polarization potential approximation to significantly redress this excess.

p - wave calculations indicate that triplet phase shifts continue to give good agreement between the E.P. and polarized orbital approximations (fig. 1.1) though at lower energies the unmodified form of Temkin and Lamkin shows closer coincidence. Singlet phase shift agreement is only found at very low energies. The negative higher energy behaviour of the E.P. approximation is merely suggested by the modified polarized orbital approximation.

### 3. CLOSE COUPLING.

The theory underlying close coupling methods relies on the assumption that we can find a tractable truncation to a 'complete state set' representation of the state of the scattering system. An obvious basic set with physical appeal is one based on hydrogen atom wave functions. As the nature of the interactions considered are such as to conserve orbital and spin angular momenta,  $L$  and  $S$ , and their projections,  $M_L$  and  $M_S$ , a diagonal

wave function is constructed

$$\Psi_{r'}(1,2) = R_{n l_2}(r_2) Y_{L l_1 l_2}(\hat{r}_1, \hat{r}_2) \delta_{S S_2} \quad 1.40$$

Then the incoming wave function is completely represented by

$$\Psi_{r'}(1,2) = 1/\sqrt{2} \sum_{r''} (1 \pm P_{12}) \{ \Psi_r(1,2) u_{rr'}(r_1) \} \quad 1.41$$

where  $r = (n, k_n, l_1, l_2, L, S, ML, MS)$ , and the radial functions  $u_{rr'}$  are to be determined. Its asymptotic form providing the scattering matrix  $S(r, r')$  may be written as

$$u_{rr'}(r) \sim 1/k_n \{ \delta(r, r') \exp(-i[k_n r - l_1 \pi/2]) - S(r, r') \exp(i[k_n r - l_1 \pi/2]) \} \quad 1.42$$

The truncated form of eq. 4.1 met with in practice does not satisfy the Schrodinger equation. Instead we use the projected form

$$\int \Psi_r(1,2) \{ H - E \} \Psi_{r'}(1,2) d\underline{r}_2 d\hat{r}_1 = 0 \quad 1.43$$

This gives rise to a set of coupled integro-differential radial equations

$$[d^2/dr_1^2 - l_1(l_1+1)/r_1^2 + k_n^2] u_{rr'} = \sum_{r''} \{ V(r, r'') \pm W(r, r'') \} u_{r''} \quad 1.44$$

The direct term on the right hand side is given by

$$V(r, r'') = -1/r_1 \delta_{rr''} + \sum_{\lambda} f_{\lambda}(l_1, l_2, l_1'', l_2'', L) Y_{\lambda}(R n l_1, R n'' l_1'') \quad 1.45$$

and the exchange term by

$$W(r, r'') u_{r''} = \sum_{\lambda} g_{\lambda}(l_1, l_2, l_1'', l_2'', L) \{ \delta_{\lambda 0} (E_n + E_{n''} - E) \Delta(R n'' l_1'' u_{r''}) + Y_{\lambda}(R n'' l_1'' u_{r''}) \} r_1 R_{\lambda} \quad 1.46$$

The coefficients  $g_{\lambda}$  and  $f_{\lambda}$  are tabulated, and the functions  $Y_{\lambda}$  and  $\Delta$  presented, in Percival and Seaton (1957)

### 3. CLOSE COUPLING WITH CORRELATION

While close coupling correctly determines resonance effects and threshold behaviour introduced by the long range interactions coupling different channels (Burke, Ormonde, Whitaker - 1967) it fails to allow for modifications to resonances, and the magnitude of cross sections, due to short range effects.

A model may be constructed including all significant channels plus

orthogonal short range correlation terms of the Hylleraas type, with an asymptotic cut off chosen to satisfy the correct boundary conditions. Hahn et al (1964) indicate that such a choice leads to a minimum bound on certain quantities associated with the R-matrix provided that the energy remains insufficient to excite the system into channels not explicitly included in the expansion.

Burke and Taylor (1966, 1967) applied this method to the three state approximation by writing the wave function.

$$\Psi^{(87)}(1,2) = \Psi_{1s-2s-2p}(1,2) + (1 \pm p_2) \Phi(1,2) \quad 1.48$$

$$\text{where } \Phi(1,2) = \sum_i 1/(r_1 r_2) \{ a_i \exp(-k_1 r_1 - k_2 r_2) r_1^{p_1} r_2^{p_2} r_{12}^{p_{12}} Y_{L_1 L_2 L_{12}}(\hat{r}_1 \hat{r}_2 \hat{r}_{12}) \} \quad 1.49$$

The failure of the two terms of eq.48 to satisfy the orthogonality condition required by Hahn's minimum principle could be corrected by a simple transformation of the latter term. However, substitution of either  $\Psi^{(87)}$  or its transformation into eq.43 gives an identical form.

By varying the correlation parameters, contour lines for constant sum of eigenphases were computed by Burke and Taylor for S waves at  $E = 0.81$  ryd. The minimum principle is illustrated by the non-intersection of the converging contours as more correlation is added. The bound principle is valid up to the  $n = 3$  threshold. Though the correlation terms attempt to simulate the resonance region below this threshold a more satisfactory form results by coupling in the lowest closed channels (Burke, Ormonde, Whitaker, 1967).

#### CLOSE COUPLING RESULTS

For energies below the resonance region corresponding to the  $n = 2$  threshold, results for  $S^\pm$  and  $P^\pm$  phase shifts are given in table 1.1 and fig 1.1. For singlet s-waves there is no centrifugal barrier and the symmetric wave function allows the projectile to infiltrate the atom. The importance of the inter-electron interaction makes the correlation effects of higher

channels critical. Phase shifts, with inclusion of different coupled channels, are compared with the essentially correct Schwartz values (1961) (see table 1.2.) Observing the behaviour of the 1s, 1s-2s and 1s-2p couplings we see that inclusion of either 2s or 2p coupling takes the 1s result a quarter way to the correct value. To understand the nature of the effects it is noted that while 66% of polarisation is due to the 2p-state (Castillejo (1960).), this coupling provides for a minor part of the 1s error, some of which will be due to correlation. The small polarization effect is further indicated by the small change associated with coupling to the 3p-state. The fact that the 2s-state owes nothing to polarization indicates the importance of correlation. Coupling between states within an energy level is indicated by the difference between the 1s-2s-2p correction and the sum of those of the individual 2s and 2p states. Slow convergence resulting from the inclusion of the  $n = 3$  level channels suggests that this approach is fully exploited for energies below the  $n = 2$  threshold. In the  $n = 2$  threshold region comparison between the 3-state, 6-state and 3-state plus correlation approximations is good both above, below and within the region (see fig 1.2) Taking the latter approximation as correct we find that away from the resonance region, 6-state and 3-state results are close. In the resonance region the 6-state results move closer to those of the correlation approximation. Since results below threshold are analytically extendible above, the 6-state approximation will be preferred to the 3-state for excitation cross sections to the  $n = 2$  level (see chapter 2, section (5).)

Triplet s-wave results show good agreement between one-state, 3-state and the Schwartz variational values (table 1.1). The reliability of the

one-state results indicates that correlation is well represented whilst polarization is unimportant.

Comparison of the one-state and 3-state P-wave phase shifts (fig. 1.1) with polarized orbital results indicates the small role played by polarization below the  $n = 2$  threshold. Above  $E' = 0.02$  ryd singlet and triplet 3-state values diverge, whereas had polarization been dominant their behaviour would have been the same.

THEORETICAL METHODS FOR INELASTIC SCATTERING.

(1) Born Approximation

The Born approximation provides a simple method for calculating  $e^- - H$  inelastic cross sections. It is believed to be a reliable approximation at sufficiently high energies for non-rearrangement inelastic processes. (ref. Bransden (1968).).

The exact T-matrix element (see McDowell and Coleman (1968) for a discussion of what is meant by a matrix element in a rearrangement channel) is

$$T = \langle \psi_f | V_f | \psi_i^+ \rangle \quad 2.1$$

Now given the convergence of the expansion

$$\psi_i^+ = (1 + G_0^+ V + G_0^+ V G_0^+ V + \dots) \Phi_i^+ \quad 2.2$$

the Born approximation follows by retaining only the leading term, where

$\Phi_i^+$  is a properly anti-symmetrised unperturbed initial wave function with incoming wave boundary conditions for  $e^- - H$  scattering

$$\Phi_i^+ = 1/\sqrt{2} \{ \phi_{i1}(2) F(1) \pm \phi_{i1}(1) F(2) \} S^\pm(1,2) \quad 2.3$$

where  $F(1)$  is an incoming plane wave function. The spin wave functions

are carried in  $S^\pm(1,2)$ . Hence  $T_{if}^{(a)} = \langle \psi_f | V_f | \phi_{i1}(2) F(1) \rangle \pm \langle \psi_f | V_f | \phi_{i1}(1) F(2) \rangle \quad (2.4)$

and we define the direct term as the Born and the rearrangement term as the Born Oppenheimer (B.O) amplitudes.

An alternative view of the scattering amplitude may be considered in terms of momentum space by defining the momentum wave function.

$$g_i(\underline{k}) = \int \exp(-i \underline{k} \cdot \underline{r}) \phi_{i1}(\underline{r}) d\underline{r} \quad 2.5$$

Using the inverted form of this in the Born amplitude we have

$$T_{if}^{(a)} = (1/2\pi)^6 \int d\underline{k} \int d\underline{k}' g_i(\underline{k}) g_f^*(\underline{k}') \delta(\underline{k} + \underline{k}_i - \underline{k}' - \underline{k}_f) T_{KK'}^{(a)}(1,2) \quad 2.6$$



where

$$T_{kk'}^{(B)}(1,2) = -\frac{1}{2\pi} \int d\underline{r}_1 \int d\underline{r}_2 \exp(-i[\underline{k}_f \underline{r}_1 + \underline{k}'_f \underline{r}_2]) \exp(i[\underline{k}_i \underline{r}_1 + \underline{k}_i \underline{r}_2]) \quad 2.7$$

This can be understood as an average on the energy shell of the initial and final momentum distributions of a term which is the Born approximation to  $T$  for two free particles. In the Born approximation the atomic potential  $U$  does not directly influence the scattering process, but merely serves to determine the momentum distribution of the atomic electron.

The validity of the anti-symmetrised Born approximation is restricted to high energies where the contribution from the B.O. amplitude is small. At low energies, especially near threshold, it frequently exceeds conservation limits. A comparison of excitation cross sections for the 1s-2s and 1s-2p electron induced transitions in hydrogen atoms in the Born and Born Oppenheimer (singlet and triplet) approximations is given in fig. 2.1 and fig. 2.2. In the 1s-2s process the B.O. cross sections vastly exceed the Born values largely due to the excessive triplet contributions. Convergence of the two approximations is indicated in Table 2.1 for energies in excess of 4 ryd. In 1s-2p transitions the B.O. cross sections again exceed the Born values throughout the energy range. For energies greater than 1 ryd. the singlet B.O. value exceeds the triplet slowing the convergence of the B.O. cross sections to the Born, though convergence is faster than was the case in the 1s-2s transition.

Now let us consider the evaluation of the Born cross sections in more detail. Due to the orthogonality of the initial and final state unperturbed wave function, the direct term of the scattering amplitude arising from the projectile nucleon interaction term is identically zero. The Born transition amplitude, including exchange may be written

$$T_{if}^{\pm} = \frac{1}{2\pi} \{ I_2 \pm (I_3 - I_1) \} \quad 2.8$$

where

$$I_1 = 2\pi \langle \psi_i(1,2) | \frac{1}{r_{12}} | \psi_i(2,1) \rangle \quad 2.9$$

$$I_2 = 2\pi \langle \psi_i(1,2) | \frac{1}{r_{12}} | \psi_i(1,2) \rangle \quad 2.10$$

$$I_3 = 2\pi \langle \psi_i(1,2) | \frac{1}{r_{12}} | \psi_i(2,1) \rangle \quad 2.11$$

TABLE 2.1

Cross Sections for (1s-2s) inelastic scattering ( units -  $\pi a_0^2$  )

<u>k<sup>2</sup>(ryd)</u>	<u>Born</u>	<u>B.O.</u>	<u>Rudge</u>	<u>Qp</u>
0.77	0.110	1.34		
0.80	0.162	1.83		
0.85	0.207	2.04		
0.90	0.230	1.98		
1.00	0.248	1.65	0.019	0.99
1.10	0.251	1.30		
1.44	0.228	0.60		
2.00	0.183			0.59
2.25	0.167	0.204	0.047	
4.00	0.102	0.096	0.042	
5.00	0.083			0.19
9.00	0.048	0.045	0.031	
10.00	0.043			0.078
16.00	0.027	0.026	0.021	
20.00	0.022			0.033
100.00	0.0044			0.0053

Born and Born-Oppenheimer (present calculation)

Rudge = Ochkur approximation (1965)

Qp = Impulse approximation with a peaking approximation (Coleman and McDowell 1966)

TABLE 2.2.

Cross Sections for  $1s-2p$  Scattering (units- $\pi a_0^2$ )

<u><math>k^2</math> (ryd)</u>	<u>Born</u>	<u>B.O.</u>	<u>QP</u>
0.77	0.34	1.42	
0.80	0.53	1.88	
0.85	0.73	2.01	
0.90	0.86	1.92	
1.00	1.04	1.66	4.0
1.50	1.28		
2.00	1.31		4.7
2.50	1.25		
4.00		0.97	
5.00	0.93		2.6
9.00	0.66	0.65	
10.00	0.61		1.4
16.00	0.45	0.45	
20.00	0.37		0.7
100.00	0.094		0.13

Rather than determine the transition amplitudes directly as a function of momentum transfer, with cross sections following from eq. 0.22, it is often more convenient to employ a partial wave expansion of the transition amplitude. The integration over the angular coordinate  $\hat{k}$  is simply effected to provide  $Q(i \rightarrow f)$  (see eq. 0.21). The resulting cross sections are expressed as a series of partial cross sections. This is illustrated below for the Born approximation.

Before proceeding with the reduction of the transition amplitude it will be convenient to introduce some notation. The atomic wave function is a product of a spherical harmonic function and a radial function, normalised to unity

$$\psi_i(\mathbf{r}) \equiv \psi_{nlm}(r) = R_{nl}(r) Y_{lm}(\hat{r}) \quad 2.12$$

where

$$Y_{lm}(\hat{r}) = P_{lm}(\cos \theta) \exp(im\phi) \sqrt{(2l+1)/4\pi} \quad 2.13$$

$P_{lm}$  is a Legendre polynomial. The  $i^{\text{th}}$  electron has the position vector

$$\underline{r}_i = (r_i, \theta_i, \phi_i) \text{ in a frame fixed in space. } F(1), \text{ the projectile wave}$$

function, can be expanded in Legendre polynomials and corresponding radial functions defined by

$$F(1) = \sum_{s=0}^{\infty} (i)^s u_s(r) P_{s0}(\hat{r}). \quad (2s+1) \quad 2.14$$

normalised such that in the absence of any interactions  $u_s$  reduces to a spherical bessel function  $j_s$  with the asymptotic behaviour

$$j_s(kr) \underset{r \rightarrow \infty}{\sim} \sin(kr - s\pi/2) / (kr) \quad 2.15$$

The projectile wave function then reduces to a plane wave

$$F(1) = \exp(i \underline{k} \cdot \underline{r}) \quad 2.16$$

The interaction potential  $V$  may be expanded in terms of Legendre polynomials of the interelectronic coordinate.

$$V = \sum_{s=0}^{\infty} \gamma_s(1,2) P_{s0}(\hat{r}_{12}) = 1/r_1 \quad 2.17$$

where

$$\gamma_s(1,2) = r_1^s / r_2^{s+1} \quad 2.18$$

$r_1$  and  $r_2$  being the lesser and greater of  $r_1$  and  $r_2$ .

The Born approximation is equivalent to taking only the direct term of eq.2.8 and replacing the projectile wave function by a plane wave. It will be convenient to use it to illustrate the partial cross section approach. More complicated approximations will be developed in a parallel manner. Substituting eq.2.12 to 2.15 into the Born format and noting that the radial functions are real, gives

$$I^{(s)} = \int d\mathbf{r}_1 \exp(-i\mathbf{k}_i \cdot \mathbf{r}_1) \exp(i\mathbf{k}_f \cdot \mathbf{r}_1) \int d\mathbf{r}_2 \cdot \frac{1}{r_2} \cdot \delta_i(z) \delta_f(z) \\ = \int \left\{ (-i)^{s'+s} \langle s' l' m' | \lambda \mu | s' 0 \rangle \langle l' m' | \lambda \mu | l m \rangle (4\pi)^{3/2} (2s'+1)^{1/2} Y_{s' l'}(\hat{\mathbf{r}}_1) \right. \\ \left. \cdot \int d\mathbf{r}_1 r_1^2 j_s(k_f r_1) \int s'(k_i r_1) \int d\mathbf{r}_2 r_2^2 R_f(r_2) R_i(r_2) \delta_{i,2} \right\} \quad 2.19$$

where

$$\delta_f(z) = R_f(r_2) Y_{lm}(\hat{\mathbf{r}}_2) \quad \text{and} \quad \delta_i(z) = R_i(r_2) Y_{l'm'}(\hat{\mathbf{r}}_2)$$

The preferred frame of reference is taken to be a cartesian frame Oxyz with z axis along the direction of the incident particle momentum ( $\hat{\mathbf{k}}_i = \mathbf{z}$ )

The coefficients

$$\langle l'' m'' | l' m' | l m \rangle = \int \sqrt{4\pi/(2l+1)} d\hat{\mathbf{r}} Y_{l'' m''}(\hat{\mathbf{r}}) Y_{l' m'}(\hat{\mathbf{r}}) Y_{lm}(\hat{\mathbf{r}}) \quad 2.20$$

can be expressed in terms of Clebsch-Gordon coefficients,  $C_{m'' m' m}^{l'' l' l}$ ,

by

$$\langle l'' m'' | l' m' | l m \rangle = \left[ (2l+1)/(2l''+1) \right]^{1/2} C_{0 \ 0 \ 0}^{l'' \ l' \ l} \cdot C_{m'' \ m' \ m}^{l'' \ l' \ l} \quad 2.21$$

The C.G coefficients have been tabulated (e.g. Condon and Shortley (1935)).

The total cross section is

$$Q(i \rightarrow f) = k_f / (4\pi k_i) \int |I^{(s)}|^2 d\hat{\mathbf{k}}_f \quad (a_0^2) \quad 2.22$$

### 1s-2s Scattering

This involves scattering between states of the same angular momenta ( $l = l' = 0$ ;  $m = m' = 0$ ). The Born amplitude becomes

$$I^{(s)} = \sum_{s'=0}^{\infty} (4\pi)^{3/2} (2s'+1)^{1/2} \int_0^{\infty} d\mathbf{r}_1 r_1^2 j_s(k_f r_1) \int s'(k_i r_1) \int_0^{\infty} d\mathbf{r}_2 r_2^2 R_{1s}(r_2) R_{2s}(r_2) \delta_{0,2} Y_{s0}(\hat{\mathbf{r}}_2) \quad 2.23$$

The total cross section follows, integrating over the final momentum coordinate  $\hat{\mathbf{k}}_f$

$$Q^{(s)}(1s \rightarrow 2s) = 16 k_f / k_i \sum_{s'=0}^{\infty} (2s'+1) |P_s^{(s)}(1s \rightarrow 2s)|^2 \quad (\pi a_0^2) \quad 2.24$$

where

$$P_3^{(2)}(1s \rightarrow 2s) = \int_0^\infty dr_1 r_1^2 j_s(k_f r_1) j_s(k_i r_1) \int_0^\infty dr_2 r_2^2 \delta_0(1,2) R_{1s}(r_2) R_{2s}(r_2) \quad 2.25$$

The inner integral gives

$$\int_0^\infty dr_2 r_2^2 \delta_0(1,2) R_{1s}(r_2) R_{2s}(r_2) = \sqrt{8}/27 \cdot \exp(-3r_1/2) (2+3r_1) \quad 2.26$$

The outer integral is evaluated numerically. Fast convergence of the integrand is assured by the exponential nature of the inner integral.

Extending the system to incorporate exchange in the manner of eq. 2.8, summing over spin states provides the Born Oppenheimer cross sections

$$Q(1s \rightarrow 2s) = 4k_f/k_i \sum_{s=0}^\infty \left\{ |P_3^+(1s \rightarrow 2s)|^2 + 3 |P_3^-(1s \rightarrow 2s)|^2 \right\} (\pi a_0^2) \quad 2.27$$

where the scattering amplitudes corresponding to singlet and triplet states are

$$P_3^\pm(1s \rightarrow 2s) = \int_0^\infty dr_1 r_1^2 j_s(k_i r_1) e^{-r_1/2} (1/2)^{3/2} * \left\{ \pm (2-r) \left[ \frac{2\delta_{s0}}{(1+k_+^2)} - \frac{J_{kf}^{(s)}(r)}{(2s+1)} \right] - 8/27 \cdot e^{-r} j_s(k_f r) (2+3r) \right\} \quad 2.28$$

$$\text{and } J_{kf}^{(s)}(r) = \int_0^\infty dr_2 r_2^2 j_s(k_f r_2) \delta_s(1,2) R_{1s}(r_2). \quad 2.29$$

### 1s-2p Scattering

This involves scattering between states whose initial and final angular momenta differ by one ( $l=1; m=\pm 1, 0; l'=0; m'=0$ ). Full exchange total cross sections follow, summing over all final states.

$$Q(1s \rightarrow 2p) = 4k_f/(3k_i) \sum_{s=0}^\infty \left\{ |P_3^+(1s \rightarrow 2p)|^2 + 3 |P_3^-(1s \rightarrow 2p)|^2 \right\} (\pi a_0^2) \quad 2.30$$

Each partial cross section corresponds to a term in the partial wave expansion of the initial state.

$$|P_3^\pm(1s \rightarrow 2p)|^2 = \left\{ s \cdot H^\pm(s-1, s)^2 + (s+1) \cdot H^\pm(s+1, s)^2 \right\} / (2s+1) \quad 2.31$$

where

$$H^\pm(\lambda, s) = \int dr_1 r_1^2 j_s(k_i r_1) (1/2)^{3/2} * \left\{ b^4/(81 r_1^4) [8 - e^{-3r_1/2} (8 + 12r_1 + 9r_1^2 + 27r_1^3/8)] j_\lambda(k_f r_1) \right. \\ \left. \pm r_1 e^{-r_1/2} \left[ 3 J_{kf}^{(\lambda)} - \frac{2 \delta_{s1} \delta_{\lambda 0}}{(1+k_+^2)} \right] / (2\lambda+1) \right\} \quad 2.32$$

The two terms of eq.31 refer to the situations in which the final angular momentum of the projectile is increased ( $\lambda = s + 1$ ) or decreased ( $\lambda = s - 1$ ) by one unit. Cross sections for scattering to states of different magnetic quantum number are  $m$  dependent, and involve products of mixed terms of  $H^{\pm}(s + 1, s)$  and  $H^{\pm}(s - 1, s)$ . Summation over the final states causes complete cancelation of these mixed terms.

The Born approximation is provided by dropping the exchange terms of eq.32. Note that this makes  $|P_s^{+}|^2$  and  $|P_s^{-}|^2$  identical.

The integral over  $r_1$  in eq.32 can be evaluated numerically. All terms of the integrand but one direct term are modified by an exponential decay function. Convergence is satisfied in general by taking an upper limit  $r = 40$  a.u. The leftmost direct term of the integrand goes as  $j_{\lambda}(k_1 r_1) j_{\lambda}(k_2 r_1)$ , and must be integrated out until some convergence condition is satisfied (see Chapter 6). As a check on the new cross sectional calculations discussed later, total Born and B.O. cross sections have been found using partial cross sections evaluated numerically in both  $1s-2s$  and  $1s-2p$  transitions. In the energy range considered, 0 - 3 ryd, comparison was made with total cross sections evaluated by numerical integration over momentum transfer after the fashion of eq. 0.22. This comparison indicated that, provided sufficient partial waves were included, an accuracy to at least the fifth figure could be expected. For  $1s-2s$  cross sections this required seven partial wave contributions at 2 ryd in both Born and B.O. summations, whilst for  $1s-2p$  cross sections nine partial wave contributions were required even as low as 1 ryd.

## (2) Ochkur Approximation.

The deficiency of the B.O. approximation at low energies is well known. Ochkur (1964) argues that if the exchange amplitude is expanded in inverse

powers of the incident particle momentum  $k_i$ , then only the first term of the series is consistent with first order perturbation theory. At low energies the higher order terms cease to be small and the outcome is meaningless. In the Ochkur approximation these terms are dropped, leaving only the electron-electron interaction to make an explicit contribution to the scattering matrix.

The failure of the B.O. approximation is to some extent due to the non-orthogonality of the initial and final states leading to spuriously large terms in the transition amplitude. Though the Ochkur approximation gives smaller results, its derivation is unsatisfactory. Rudge (1965) chose a trial function in the Kohn variational principle, eq. 0.37, satisfying the correct boundary conditions such that substitution into the B.O. format yields the Ochkur approximation. In choosing the scattered particle wave function  $f(r)$  to have the form

$$\phi_0(r) f(r) = - \nabla^2 \{ \phi_0(r) \exp(i \underline{k}_n \cdot \underline{r}) \} / (k_n - i)^2 \quad 2.40$$

the ensuing wave function satisfies the orthogonality condition.

Cross sections for 1s-2s transitions are shown in fig 2.3 (Rudge 1965) comparing well in shape and magnitude with the results of Stebbings (1960). However recent work of Fite(1968) suggests that the Stebbings results should be renormalized to a maximum of  $0.18(\pi a_0^2)$ . The Rudge results are then too low by a factor of two at all energies. Comparison with the Born approximation, table 2.1, indicates the convergence at higher energies.

### (3) Impulse Approximation

The basic assumption of the impulse approximation is that the binding forces in the target play no other role in the collision than to determine the momentum, distribution of the bound particle before the collision.



This assumption seems reasonable if the duration of the collision is short compared with the characteristic period of the target. Since binding forces play no direct role the struck particle may be regarded as free, reducing the problem to a two body one. Unlike the Born approximation, the interaction between the projectile and target is not assumed small here, but is treated exactly to all orders.

If the impulse approximation to the T-matrix replaces the Born T-matrix in eq.6, then (7) differs in the replacement of the plane wave, representing the initial state, by a wave function  $\psi_{12}$  satisfying

$$(-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 + \frac{1}{r_{12}} - \epsilon) \psi_{12}(\underline{k}_1, \underline{k}) \quad 2.50$$

$\epsilon$  being the energy corresponding to  $\underline{k}_1$  and  $\underline{k}$ , the relative momenta of electrons (1) and (2). This equation provides an exact solution, a product of a plane wave representing the motion of the centre of mass of the electrons and a hypergeometric function representing their relative motion. Using properties of Fourier transforms the new amplitude reduces to

$$T_{if}^{(imp)} = - (\frac{1}{2}\pi)^4 \int d\underline{r}_1 \int d\underline{r}_2 \exp(-i\underline{k}_1 \underline{r}_1) \phi_i^*(z) \cdot V \int d\underline{k} g_i(\underline{k}) \psi_{12}(\underline{k}_1, \underline{k}) \quad 2.51$$

Comparison of this expression with the exact amplitude shows that the impulse approximation is equivalent to replacing  $\Psi(\text{exact})$  by the wave function

$$\Psi^{(imp)} = (\frac{1}{2}\pi)^3 \int d\underline{k} g_i(\underline{k}) \psi_{12}(\underline{k}_1, \underline{k}) \quad 2.52$$

To give a more exact treatment the approximation should also include the interaction between the projectile and the centre of force. For heavy particle impact a canonical transformation avoids this requirement giving rise to a phase factor leaving transitions unaffected. At high energies where the Born approximation holds good, the extra terms may be ignored even for electron scattering. At low energies and with electron scattering

such a neglect is a very dubious step.

Akerib and Borrowitz (1961) attempted to apply the impulse approximation to electron hydrogen scattering. Their calculated 1s-2s excitation cross sections were far too small but 1s-2p and ionisation cross sections gave reasonable agreement with experiment. Apart from objections arising from the application of the impulse approximation to electron scattering (neglect of exchange and the electron-nucleon interaction) they made mathematical errors which suggest that any agreement with experiment is fortuitous. (Coleman and McDowell 1966, and Coleman and Economides 1969).

Consider a problem in which a particle of charge  $Z$  is scattered by a hydrogen atom. This leads to a solution of eq.50.

$$\psi_{12}(\underline{k}, \underline{k}) = (1/2\pi)^3 \exp(i[\underline{k}_f \cdot \underline{R} + \underline{k}_i \cdot \underline{R}]) \exp(\pi z/\kappa) \cdot \Gamma(1 - 1/2 iz/\kappa) F_1(1/2 z/\kappa, 1, i[\underline{k}_f - \underline{k}_i] \cdot \underline{R}) \quad (2.53)$$

The normalisation chosen by Akerib and Borrowitz differs by a factor  $1/\kappa$ , a non-trivial difference since cross sections result from integration over  $k$ . That eq.53 is correct shows in the limit  $z \rightarrow 0$ ,  $\psi_{12}$  reducing to the equivalent Born function.

Substituting  $\Psi_i^{(imp)}$  into the transition amplitude gives

$$T_{if}^{(imp)} = 2/(\pi^3 p^2) \int d\underline{k} N(k) g_f([\underline{k} + \underline{k}_i]/2) g([\underline{k}_f + \underline{k} - 2\underline{k}_i]/2) \frac{[(\underline{p} + \underline{k})^2 - k^2]^{-1/2}}{p^2} \quad (2.54)$$

where  $\underline{p} = \underline{k}_f - \underline{k}_i$  and  $N(k)$  is a normalization factor. The factor

$g(\underline{t})$  is sharply peaked about  $\underline{t} = 0$ . A peaking approximation results on replacing the remainder of the integrand (assumed slowly varying) by its value at  $\underline{t} = 0$ .

Coleman and McDowell (1966) have evaluated 1s-2s and 1s-2p cross sections for electron impact correcting the errors of Akerib and Borrowitz (see table 2.1 and 2.2) The approximation shows correct agreement with the Born approximation at high energies though the approach to the limit is

slow. Furthermore the results are considerably higher than the Born values at moderate and low energies and bear no resemblance to the results published by Akerib and Borrowitz. Coleman (1967) has shown that the poor results are obtained as a result of a drastic peaking approximation. Apart from a more accurate determination of the triple  $k$  integral, extension of the approximation to include exchange and projectile nucleon forces seems in order.

#### (4) Vainshtein Approximation for $e^-$ - H Scattering

The total wave function is chosen as a product of an unperturbed hydrogen atom wave function and a function  $g$  of coordinates  $\rho$  and  $R$

$$\Psi^{(\nu)}(1,2) = \phi_i(2) g(\rho, R) \quad 2.60$$

so that the Schroedinger equation provides the exact equation

$$[\nabla_R^2 + \nabla_\rho^2 + \gamma/R - \gamma/\rho + k_0^2] g(\rho, R) = Q g(\rho, R) \quad 2.61$$

where

$$Q = [\gamma/R - \gamma/\rho - \frac{1}{R} - \frac{1}{\rho} - 2V_i \ln \phi_i(2) \nabla_\rho \ln g(\rho, R) + (1-\gamma)/\rho] \quad 2.62$$

For the present we take  $\gamma = 1$

The Vainshtein approximation supposes that  $Qg$  is zero. The resulting solution of  $g$  satisfying the correct boundary conditions is a product of attractive and repulsive coulomb functions of  $R$  and  $\rho$  respectively.

Expressing  $\phi_i(2)\phi_f(2)$  in terms of its Fourier transform  $\tilde{\phi}$ ,

replacement of the exact wave function in eq.1 by  $\Psi^{(\nu)}(1,2)$  gives

$$T_{if}^{(\nu)} \propto \int d\underline{s} \tilde{\phi}(\underline{p} - \underline{s}) \int d\underline{R} \exp(i\underline{s} \cdot \underline{R}) F(\nu, 1, i[k_i R - k_f R]) \quad 2.63$$

$$\times \int d\underline{\rho} / \rho \cdot \exp(i[2\underline{p} - \underline{s}] \cdot \underline{\rho}) F(\nu, 1, i[k_i \rho - k_f \rho])$$

where  $\underline{p}$  is the projectile momentum transfer and  $\nu = \gamma/k_i$ . The contribution from the electron nucleon interaction potential has been ignored.

As the integral with respect to  $\underline{R}$  is unbounded as  $s \rightarrow 0$ , a peaking

approximation is applied. That is, it is noted that the exponential factors have stationary phases about  $\underline{s} = 2p$ , replacing the slowly varying  $\tilde{\mathcal{D}}(p - \underline{s})$  by  $\tilde{\mathcal{D}}(p)$ . In Vainshteins paper (1964) the integration is facilitated on replacing  $\exp(i[2p - \underline{s}]\rho)$  by  $\exp(i[2p + \underline{s}]\rho)$ . As  $\tilde{\mathcal{D}}(0) = 0$ , the error in the peaking approximation in the region  $\underline{s} \sim p$ , is suggested as a compensating effect. Crothers and McCarrol (1965) were critical of this step and therein lies the motivation of their alternative approach. The integration was completed by means of a method suggested by Nordseick (1954). Instead of using the prior transition amplitude used by Vainshtein et al, Crothers and McCarrol consider the post form

$$T_{if}^{(cm)} = \langle \Psi_f^{-(\nu)} | V | \psi_i \rangle \quad 2.64$$

and carry out a parallel analysis avoiding the unsatisfactory step of changing the sign of the exponential term.

To investigate further the neglected terms  $Qg$  we seek its form for large  $\rho$  and  $R$  and arbitrary  $\gamma$ . The post form provides

$$Q = \gamma/R - 2/(R + \rho) + (1 - \gamma)/\rho + i\nu\sqrt{\epsilon}(\gamma_R + \gamma_\rho) + O(1/\rho^2) + O(1/R^2) \quad 2.65$$

where  $\epsilon$  is the ionisation potential of the level  $f$ . Amongst these terms is one depending on  $\nu$ , which diverges in the region of the excitation threshold. By choosing the effective charge of the complex form  $\gamma = k_f / (k_f - i\sqrt{\epsilon})$ , not only is this divergence removed but also all discarded terms are then of order greater than  $1/\rho$ .

Keeping both exchange and effective charge the Crothers and McCarrol approach shows excellent agreement with the unrenormalized experimental results of Stebbings (1960) (1s-2s) and Fite (1959) (1s-2p) (see fig. 2.4). Apparently though exchange effects are negligible, effective charge variations produce significant changes in both magnitude and shape. High

energy behaviour is in line with the good behaviour of the Born cross sections.

Omridvar attempted to correct errors in the Vainshtein et al analysis avoiding the change in sign of  $(2i\epsilon/\rho)$ . Crothers (1967) and Peach (1967) showed that Omridvar chose a faulty analytic continuation of a term in the transition amplitude. Results for the corrected evaluation of the peaking approximation in the Vainshtein et al approximation are shown in fig.2.4. The prior results exceed the Born 1s-2p cross sections at the maximum though they tend to the Born at high energies.

The philosophy behind the Vainshtein approximation appealing directly to the inter-electronic potential whilst keeping the correct boundary conditions, coupled with the good agreement shown in comparison of the Crothers and McCarroll and experimental results, provides an attractive prospect. At the same time certain features throw doubt on its reliability. Only detailed investigations of the peaking approximation will justify its usage. Such an investigation applied by Kyle and McDowell (1969) to the Coulomb Born approximation indicated an error factor of two. Further neglect of the electron nucleon interaction cannot be justified for electron scattering without more detailed investigation including this term.

#### (5) Close Coupling

The cross sections for 1s-2s and 1s-2p scattering processes have been compared by Burke, Ormonde, and Whitaker (1967) in the 3-state and six-state approximation (see fig. 2.5 and 2.6.) At low energies the dominant contributions are found to be from the singlet S, P and D and triplet P partial cross sections. (for 1s-2s values see fig 6.6. to 6.10) The good agreement between the two approximations, observed <sup>in elastic scattering</sup> below the  $n = 2$  threshold continues up to energies of about 0.83 ryd. As the energy is further increased the

expected resonances occur in the six state approximation just below the  $n = 3$  threshold. Their behaviour can be understood with the aid of the Fano expression (1961), for resonant cross sections.

$$Q_{ij} = (Q_a)_{ij} (\epsilon + q_{ij})^2 / (1 + \epsilon^2) + (Q_b)_{ij} \quad 2.70$$

where

$$\epsilon = 2(E - E_r) / \Gamma$$

$E_r$  and  $\Gamma$  are the resonance position and width, and  $q_{ij}$  the line profile which gives the resonance its shape.

All the resonances observed have two features in common. Firstly  $q \ll 1$ , implying that the resonance interferes destructively with the background cross section, whilst the small values of  $Q_b$  means that the resonance decays into a linear combination of states at the  $n = 2$  threshold excited from the ground state. Because all the  $q$ 's are small the individual resonance effects tend to enhance rather than interfere giving windows in the cross section below the  $n = 3$  threshold and depressing the cross section above it. This brings the  $Q(1s-2s)$  peak down from the three state value of  $k^2 = 1$  ryd to 0.86 in the six state approximation. This is in line with the experimental data of Lichten and Schultz (1959) and Hils (1966). Furthermore the peak value is somewhat lower at  $0.22 (\pi a_0^2)$  against  $0.36 (\pi a_0^2)$  almost in line with the peak value recommended by Fite et al (1968) of  $0.18 (\pi a_0^2)$ .

# THE POLARIZED ORBITAL METHOD FOR CONTINUUM EXCITATION CROSS SECTIONS

When exact wave functions are used for the initial and final states of the system, the dipole length and dipole velocity formula give equivalent ways of defining the dipole photoionisation cross section. It might, therefore, be expected that the accuracy of approximate wave functions will be indicated by the difference between the approximate length and velocity formula. They can be written in terms of the oscillator strength per unit energy interval in the continuum, and having the form

$$(df/d\epsilon)_L = (I + \epsilon) \left| \int \Psi_i^* (\underline{r}_1 + \underline{r}_2) \Psi_f d\underline{r}_1 d\underline{r}_2 \right|^2 \quad 2.80$$

for the dipole length formula and

$$(df/d\epsilon)_V = (I + \epsilon) \left| \frac{1}{2(I + \epsilon)} \int \Psi_i^* (\underline{v}_1 + \underline{v}_2) \Psi_f d\underline{r}_1 d\underline{r}_2 \right|^2 \quad 2.81$$

for the dipole velocity formula.

where  $I$  is the ionisation potential of the initial state of the atom and  $\epsilon$  is the ejected electron energy.

Cross sections follow using

$$Q = \int_{k_{min}}^{k_{max}} I(k) dk \quad 2.82$$

where

$$df/d\epsilon = \frac{1}{2} (I + \epsilon) \cdot \epsilon \cdot k \cdot I(k) \quad 2.83$$

The above dipole formula are using

$$\begin{aligned} \lim_{k \rightarrow 0} \frac{1}{(ik)} T_{if} &= \lim_{k \rightarrow 0} \frac{1}{(ik)} \langle \Psi_i | \sum_j e^{ikr_j} | \Psi_f \rangle \quad 2.84 \\ &= \hat{k} \cdot \langle \Psi_i | \sum_j \underline{r}_j | \Psi_f \rangle \end{aligned}$$

As such this provides the same T-matrix expression for the cross sections as applies to this thesis, though the above potential is that of an electromagnetic field.

Only the (1s) ( $\epsilon p$ ) 'P state contributes to these integral for photoionisation of Helium. Thus Bell and Kingston (1967(1)) approximated the continuum wave function by

$$\Psi_f = (2/\pi)^{1/2} [ \exp(-2r_1) f_1(\epsilon/r_1)/r_1 + \exp(-2r_2) f_2(\epsilon/r_2)/r_2 ] \quad 2.85$$

representing the ionised system with zero angular momentum about the polar axis. The radial wave functions  $f_i(\epsilon/r_i)$  are determined by the method of polarized orbitals (Sloan 1964) and are solutions of eq.1.20a and 1.21.

$\Psi_i$  was taken to be a bound state wave function normalised to unity and represented by both a 6-parameter function of Stewart and Webb (1963), (PO (1)), and a 20-parameter function of Hart and Herzenberg (1967) (PO(2)).

Oscillator strengths were compared with those of Stewart and Webb (1963) (SW), using Hartee Fock continuum wave functions and the 6-parameter wave function for  $\Psi_i$ , and those of Burke and McVicar (1965) (BM), using the close coupling approximation free state wave functions and the 20-parameter wave function for  $\Psi_i$ . (See table 2.3).

It is noted that by choosing the final state wave function as

$$\Psi_f = (1 \pm P_{12}) \psi_{10}(2) F(1) \quad 2.86$$

where

$$F(1) = \sum_s u_s(r)/(k^s r_1) \cdot P_s(\hat{r}) \quad 2.87$$

with  $u_s$  taken to be polarized orbitals, and including the dipole ( $s = 1$ ) term as the only non-vanishing contribution, the model is essentially the same as the single particle polarization form of chapter 6.



TABLE 2.3 OSCILLATOR STRENGTH.

Energy	DIPOLE LENGTH				DIPOLE VELOCITY			
	SW	PO(1)	PO(2)	BM	SW	PO(1)	PO(2)	BM
0.1								
0.2	7.92,-1	8.15,-1	8.02,-1	7.78,-1	7.58,-1	8.30,-1	8.29,-1	7.63,-1
1.0	4.44,-1	4.51,-1	4.48,-1	4.35,-1	4.18,-1	4.58,-1	4.59,-1	4.25,-1
8.0	2.36,-2	2.51,-2	2.53,-2		2.19,-2	2.41,-2	2.39,-2	
64.	6.27,-5	4.72,-5	5.18,-5		6.19,-5	6.38,-5	6.48,-5	

It can be seen that there is little difference between the 6-parameter and 20-parameter polarized orbital values and little to be gained by further improvements of the bound state wave function without considerable improvements in the continuum wave function.

The superiority of the polarized orbital method wave function over the Hartree Fock wave function is suggested by the fact that the difference between the former length and velocity calculations are about 50% of the difference for the latter calculations. (The difference is of course zero if the ~~wave functions are exact~~). Comparison of the polarized orbital differences with those of the close coupling approximation values do not demonstrate the superiority of either model.

To obtain an independent check on the accuracy of the calculations, oscillator strength sum rules have been evaluated by Bell and Kingston, with exact calculations of Pekeris (1959) and Pekeris and Schiff (1964) to provide

$$I_1 = \int_0^\infty (df/d\epsilon) / (I + \epsilon) d\epsilon \sim 0.488 \quad 2.88$$

$$I_2 = \int_0^\infty (df/d\epsilon) d\epsilon \sim 1.573$$

$$I_3 = \int_0^\infty (df/d\epsilon) (I + \epsilon) d\epsilon \sim 7.48$$

The corresponding values using oscillator strengths calculated using polarized orbitals and 20-parameter bound state wave functions are

	$I_1$	$I_2$	$I_3$
length	0.504	1.63	7.66
velocity	0.514	1.64	7.72

This suggests that the length and velocity forms are respectively 3% and 5.5% too high at low energies and slightly more accurate at higher energies.

Similar sum rules applied to the photoionisation of singly ionised lithium (Bell and Kingston, 1967 (2)) indicate that the corresponding length formulation using Hartree Fock continuum wave functions provides slightly more accurate oscillator strengths than the polarized orbital calculation. This may be explained as follows: The polarized orbital method takes into account long range polarization effects but neglects the effect of short range correlation. This is indicated by the superiority of the length calculation, which emphasizes larger separations, over the velocity calculation which emphasizes smaller separations. The short range failure of the polarized orbital method for photoionisation of Helium is sufficiently compensated for by consideration of long range polarization to give better results than the Hartree Fock wave function calculation.

Low energy helium photoionisation length and velocity calculations are shown in fig. 2.7 in comparison with the experimental data of Samson (1964) and Lowry et al (1965). At low photon energies the results of Samson are probably more accurate than those of Lowry et al and although the theoretical calculations tend to be somewhat larger than the former, the two sets of results agree within the limits of experimental and theoretical error.

## CHAPTER 3.

### THE EXPERIMENTAL SITUATION

#### (1) 1s-2s Excitation

Measurements of the cross section for excitation of the 2s state of atomic hydrogen are shown in fig 3.1. The three available experimental results have been renormalised to facilitate direct comparison of shapes. These are seen to be fairly good considering experimental errors. Three aspects of the experimental results deserve particular notice.

- (i) The structure in very low energy range - best demonstrated by Lichten and Schultz (1959)
- (ii) The gross structure through the medium and high-energy range found by Hils et al (1966) and which seems to be reflected in the work by Stebbings et al (1960, 1961).
- (iii) The over-all energy dependence of Stebbings et al, and Hils et al departs to a remarkable extent from that predicted by the Born approximation.

The departure of the measured 2s excitation cross sections from the Born approximation is so striking that normalisation of experimental results to the theory at high energies is questionable. The usual procedure has been to normalise to the Born approximation plus a cascading correction at the highest energies for which measurements are available. Hils et al find a good fit over the energy range 200 to 500 eV, but there is an abrupt departure from the Born results below 200 eV (which does not occur for 2p excitation).

Stebbing et al found a good fit over the range from 400 to 700 eV. From consideration of their error bars it may be concluded that a reasonable fit is possible from 150 to 700 eV, which results in a higher normalisation.

But this normalisation is inconsistent with Hils et al at lower energies. Stebbings et al chose to normalise via 2p measurements to the Born approximation for 2p excitation. The measured 2p excitation cross section fits the Born approximation to a much lower energy than is the case for 2s excitation and there is less uncertainty about the cascading correction for the 2p cross section. On this basis Stebbings et al find their results for 2s excitation in the 200 to 700 eV range lies about 50% higher than the Born cross section plus cascading. Their error bars fail to overlap the Born result at the three points in this range.

Either of the above methods of normalisation leads to a value for the peak near threshold between 0.1 and 0.15 ( $\pi a_0^2$ ). In fig 2 the experimental results in the threshold region, due to Lichten and Schultz, are shown in comparison with close coupling calculations by Burke, Taylor, Ormonde and Whitaker (1967). It is the suggestion of Burke et al that normalisation to the peak at about 11.7 eV may be valid. This is based on the observation that inclusion of the higher states has a small effect on the magnitude of the cross section at the peak, where the value is  $\sim 0.22(\pi a_0^2)$ .

This normalisation of the measurements leads to values at 500 to 700 eV which are about twice as large as predicted by the Born approximation. This measured peak to high energy ratio is inconsistent with that predicted by the close coupling calculations, which presumably converges to the Born approximation at high energies. (In the case of 2p excitation the measurements of the magnitude at threshold relative to the higher energy measurements by Smith (1965) are consistent with the results of the close coupling calculation of Burke et al).

Lichten (1961) pointed out an error that had been made in data

reduction in the experiment of Stebbings et al (1961). The point in question concerned the polarization and angular distribution of Lyman- $\alpha$  radiation produced when meta-stable atoms were quenched in a weak electric field. While Stebbings et al had used a polarization fraction of unity in reducing their data, Lichten argued that a polarization fraction of zero should be used.

In preparation for extending the experiment of Stebbings, Lichten carried out an experimental check on the quench-radiation polarization. Surprisingly it was found that the polarization was not zero, <sup>and</sup> that the intensity  $I_{\pi}$  of the component with the electric field vector parallel to the direction of the quench field was weaker than the intensity  $I_{\sigma}$  of the opposite polarization. The source of the error has been reported by Fite et al (1968) as due to neglect of  $2^2P_{3/2}$  state contributions assumed to be small compared with the  $2^2P_{1/2}$  state contribution.

Fite et al suggest that the newer value of the polarization affects cross sections for excitation to the 2s state, by increasing the values approximately 10% above those of Stebbings et al (1961). Based on those data, the maximum in the cross section at approximately 12 eV would be about 0.18 ( $\pi a_0^2$ ) only about 20% below the calculation of Burke et al.

## (2) 1s-2p Excitation.

In fig 3.4 excitation functions for the  $2p \rightarrow 1s$  transition in atomic hydrogen are shown. The experimental results displayed include the results of the original measurements by Fite and Brackmann (1958), but exclude points near threshold now believed to be in error because they did not reproduce in careful measurements by Fite, Stebbings and Brackmann (1959). The results of the latter authors have also been included but have been

renormalised by a small factor to fit recent results of Long, Cox and Smith (1967). The latter authors attempted to improve on Fite et al through a strenuous effort to reduce systematic and statistical errors to the order of a few per cent but as shown in fig 3.4 the results are in complete agreement within experimental errors except for the renormalisation already mentioned. Included in the figure are perpendicular cross sections  $Q_{\perp}$  calculated using the Born approximation and 1s-2s-2p close coupling approximation (Burke Schey and Smith (1963).) together with the formula

$$Q_{\perp} = 0.918 Q_{2p} + 0.246 Q_{2p0} \quad 3.1$$

derived by Burke and Seaton (1960)

$$\text{where } Q_{2p} = 2 \cdot Q_{2p,1} + Q_{2p,0} \quad 3.2$$

$Q_{\perp}$  and  $Q_{2p}$  (which will be used in this work) are related

$$\text{through } Q_{2p} = (3 - P) Q_{\perp} / 3 \quad 3.3$$

The polarisation  $P$  satisfies (Percival and Seaton 1958)

$$P = 3(Q_{2p,0} - Q_{2p,1}) / (7Q_{2p,0} + 11Q_{2p,1}) \quad 3.4$$

The energy dependent values of  $P$  are given in fig 3.5.

The experimentally measured polarisation is defined in terms of the intensity of dipole radiation emitted by an atom after excitation. Denoting the intensity of radiation per unit solid angle, in a direction perpendicular to the electron beam direction  $OZ$ , due to electric dipoles parallel and perpendicular to  $OZ$ , by  $I_{\parallel}$  and  $I_{\perp}$  respectively, the polarisation is defined by

$$p^{(ex)} = (I_{\parallel} - I_{\perp}) / (I_{\parallel} + I_{\perp}) \quad 3.5$$

The experimental results are normalised to the Born approximation, including a small allowance for cascading at 200 eV. The measurements and the values calculated by the Born approximation seem to fit very well

above about 120 eV, and it appears that the close coupling results may fit the measured values down to about 60 eV. However, below 50 eV the departure of the close coupling results is striking.

Some intensive calculations have been carried out in the immediate vicinity of threshold by Burke, Ormonde, Taylor and Whitaker (1967). These authors show that inclusion of close coupling to the  $n = 3$  level does not produce much of a change in the cross section at energies below the resonance region of the  $n = 3$  threshold. However it may be that at higher energies the difference between the  $1s-2s-2p$  close coupling approximation results and observed behaviour of the cross section would be accounted for by the cumulative effect of coupling to all the discrete levels with  $n \geq 3$  and the continuum states. Chamberlain, Smith and Heddle (1964) studied the behaviour of the  $2p$  excitation cross section in the neighbourhood of the threshold. They obtained experimental points for  $Q_1$  shown in fig. 3.3. Also shown is a curve based on recent calculations for  $Q_1$  by Burke et al. The dashed curve shows the result of folding the experimental energy distribution from Chamberlain et al into the theoretical curve. (The experimental points have been scaled on the abscissa and shifted on the ordinate, this being allowable within reasonable limits since no accurate determination was made of the contact potentials involved). The resulting fit is quite good. Also shown in the figure are some points obtained by Fite Stebbings and Brackman (1959) from their measurement of the threshold behaviour. While their results do not reveal the threshold structure, they are consistent with the results of Chamberlain et al when account is taken of a larger energy distribution and larger error bars.

# CHAPTER 4.

## AN INVESTIGATION OF THE POLARIZED ORBITAL APPROXIMATION FOR $e^- - H$ ELASTIC SCATTERING.

### 1) Theory of Scattering Equations. (After Callaway et al - 1968)

Consider an expansion of the total wave function  $\Psi^{(1,2)}$  in terms of the complete set of unperturbed target eigenfunctions  $\phi_n^{(0)} \equiv \phi_n$

$$\Psi^+(\underline{r}, \underline{r}_2) = 1/\sqrt{2} (1 \pm P_{12}) \sum_{n=0}^{\infty} \phi_n^{(0)}(\underline{r}_2) F_n(\underline{r}) \quad 4.1$$

Such an expansion is exact but intractable. A truncated version of it leads to close coupling approximations. Alternatively we may expand in terms of the complete set of perturbed target wave functions  $\gamma_n(\underline{r}, \underline{r}_2)$

$$\Psi^+(\underline{r}, \underline{r}_2) = 1/\sqrt{2} (1 \pm P_{12}) \sum_n \gamma_n(\underline{r}, \underline{r}_2) f_n(\underline{r}) \quad 4.2$$

$$\text{where } \gamma_n(\underline{r}, \underline{r}_2) = \phi_0^{(0)}(\underline{r}_2) + \phi_0^{(1)}(\underline{r}, \underline{r}_2) \quad \text{if } n=0 \quad 4.3$$

$$\text{and } \gamma_n(\underline{r}, \underline{r}_2) = \phi_n^{(0)}(\underline{r}_2) \quad \text{otherwise.} \quad 4.4$$

Truncating this expansion at the first term, and assuming the zero state non-degenerate,

$$\Psi^+ \simeq \Psi_0^+ = 1/\sqrt{2} (1 \pm P_{12}) [\phi_0^{(0)}(\underline{r}_2) + \phi_0^{(1)}(\underline{r}, \underline{r}_2)] f_0(\underline{r}) \quad 4.5$$

where  $\phi_0^{(0)}(\underline{r}_2)$  is the hydrogen ground state wave function and  $\phi_0^{(1)}(\underline{r}, \underline{r}_2) \equiv \phi_0^{(1)}$  is the corresponding first order perturbed orbital satisfying <sup>the</sup> perturbation equation.

$$(H_{02} - E_0) \phi_0^{(1)}(\underline{r}, \underline{r}_2) = [\tilde{V} - V] \phi_0(\underline{r}_2) \quad 4.6$$

This has certain advantages

- i) The p-character of  $\phi_0^{(1)}$  gives the polarization, exactly if the  $\phi_n^{(0)}$  are known exactly.
- ii) In each  $l$  component of  $\phi_n^{(1)}$  some continuum is included.

The variational treatment is equivalent to replacing the exact wave function by the trial form of eq.5 and projecting back onto the (first



order) perturbed atomic orbital (eq.3)

$$\int \{ \chi_0(r_1, r_2) \{ H - E \} (1 \pm P_{12}) \chi_0(r_1, r_2) + f(r_1) \} d\mathbf{r}_{12} = 0 \quad 4.8$$

This has been shown by Hahn et al (1964) to lead to a bound on certain physical measurables of the low energy scattering process.

There exists a certain ambiguity in the definition of  $\chi_0^{(1)}(1,2)$ . The unperturbed atomic wave function can be added arbitrarily without contradicting eq.6. By choosing  $\chi_0$  and  $\chi_0^{(1)}$  to be orthogonal the ambiguity is removed (cf Reeh (1961)). However Callaway et al (1968) have shown that not only does this lead to neglect of terms which <sup>are</sup> not strictly higher than second order but also leads to difficult dynamic terms. The preferable alternative insists on the normalisation to unity of the first order perturbed atomic wave function, which requires that

$$2 \int \chi_0(r_1) \chi_0^{(1)}(r_1, r_2) d\mathbf{r}_2 + \int |\chi_0^{(1)}(r_1, r_2)|^2 d\mathbf{r}_2 = 0 \quad 4.9$$

We have used the fact that the wave functions are real.

This step is essential to the optical potential model of Callaway. However it has been demonstrated that by rewriting the free particle function (see eq.1.39) essentially identical phase shifts result from either choice of  $\chi_0^{(1)}(1,2)$ . Considering only direct terms the variational expression (eq.7) gives

$$\int \chi_0^*(1,2) \{ E_0 - \frac{1}{2} \nabla_1^2 + V - E \} \chi_0(1,2) d\mathbf{r}_2 + f(1) + \int \chi_0^*(1,2) \{ \tilde{V} - V \} \chi_0(2) d\mathbf{r}_2 + f(1) = 0 \quad (4.1)$$

where the second term results from applying eq.6. Using the normalisation condition (eq.9) the projectile kinetic energy operator term gives

$$-\frac{1}{2} \{ \nabla_1^2 - \frac{1}{2} \nabla_1^2 \int |\chi_0^{(1)}|^2 d\mathbf{r}_2 - \frac{1}{2} \int |\chi_0^{(1)}|^2 \nabla_1^2 d\mathbf{r}_2 + \int \chi_0^{(1)} \nabla_1^2 \chi_0^{(1)} d\mathbf{r}_2 \} \quad 4.11$$

Ignoring terms of higher than second order (e.g.  $\int \chi_0^{(1)} V \chi_0^{(1)} d\mathbf{r}_2$ ) eq.10 simplifies to

$$-\frac{1}{2} \{ \nabla_1^2 + k_0^2 - 2 V_{pol}(1) - 2 \tilde{V}(1) + V_d(1) \} f(1) = 0 \quad 4.12$$

where  $k_0^2 = E - E_0(r_1 \alpha)$ .

The polarization potential is well known from previous work on adiabatic theory

$$V_{pol}(\underline{r}) = \int \phi_0(z) \cdot V \cdot \phi^{(1)}(1, z) d\underline{r}_2 \quad 4.13$$

The dynamic term is

$$V_d(\underline{r}) = \int |\nabla \cdot \phi^{(1)}(1, z)|^2 d\underline{r}_2 \quad 4.14$$

Callaway et al (1968) derive their approximation on lines suggested by Feshbach's projection operator formalism. It has not proved possible to find a projection operator consistent with a full second order treatment including exchange. Feshbach has derived a lower order approximation using the projection operator for the  $N$  electron atom

$$P' = (N+1)^{-1/2} A \phi_0(\underline{r}_2) \phi_0^*(\underline{r}_2') A (N+1)^{1/2}$$

where

$$A = 1 - \sum_{j=1}^N P_{S_j}$$

resulting in the central field exchange approximation. The full second

order treatment is approximated by an essentially ad hoc result using the full second order direct terms of eq.12 whilst keeping only lower order exchange terms.

The additional terms arising from the inclusion of exchange are, to lowest order in the atomic wave function

$$X_0^{\pm} = \pm \int \phi_0(z) [H - E] \phi_0(1) f(z) d\underline{r}_2 \quad 4.15$$

Let us consider the form of the single particle wave function  $f(1)$  as an expansion of spherical harmonic functions and corresponding reduced radial functions

$$f(1) = \sum_{l=0}^{\infty} u_l(r)/r \cdot Y_{l0}(\hat{r}) \quad 4.16$$

Substituting this into the direct variational expression (eq.12) and projecting out onto the  $l$ th spherical harmonic function gives rise to a set of uncoupled second order differential equations

$$L_l u_l(r) \equiv \left[ \frac{d^2}{dr^2} + k_0^2 - l(l+1)/r^2 - 2\tilde{V}(r) - 2V_{pol}(r) + V_d(r) \right] u_l(r) = 0$$

Here we have used the non-angular dependent character of the potential terms (see next section). This frees the equations from coupling terms.

Substitution of eq.16 into the exchange term and using the Hermitian nature of  $H_{02}$  gives a zeroth order term with only the zero partial wave,

$$(2E_0 - E) \int \phi_0(2) u_0(2)/r_2 \cdot dr_2 \phi_0(1) \chi_0(r_1) \quad 4.18$$

and a first order term

$$\sum_{l=0}^{\infty} \int \phi_0(2) \delta_l(1,2) u_l(2)/r_2 P_l(r_1) \chi_l(r_1) dr_2 \quad 4.19$$

where  $\delta_l(1,2)$  is the  $l^{th}$  term of the Legendre polynomial expansion of  $V$ . Projecting the exchange terms onto the  $l^{th}$  spherical harmonic function the full variational equation gives

$$L u_l(1) = \pm \chi_l(1,2) r_1 R_l(1) \quad 4.20$$

where  $\chi_l(1,2) = \{ (E_0 - k^2) \delta_{l0} \int R(r_2) u_l(r_2) r_2 dr_2 \} + \{ 2/(2l+1) \int R(r_2) u_l(r_2) \delta_l(1,2) r_2 dr_2 \}$   
 $R(2)$  is the normalised radial part of  $\phi_0(2)$ . The energies  $E_0, k^2$  are in Rydbergs. It is noted that the second exchange integral is kept as a first order term whilst other exchange distortion terms of the same order are neglected.

Though a full second order exchange approximation will not be attempted here it is interesting to compare the higher order exchange terms with the Temkin - Sloan equivalents, the two terms being derived in a parallel manner. The full exchange expression is given in appendix (1). It is noteworthy that amongst the extra terms of the present work there are no terms corresponding to Sloans velocity dependent term nor do any exchange velocity dependent terms arise. The extra terms leads to no coupling of the integro differential radial equations.

## 2) Evaluation of Polarization and Distortion Potentials

The polarization potential of an electron in the field of an electron is to be determined. It will be assumed that the motion of the electron can be ignored and terms in the wave function of order of perturbation higher

than the first will be neglected. The first order wave function is then used to calculate second order potentials.

The distorted wave function is written as a linear combination of the unperturbed hydrogen ground state wave function  $\phi_0$  and a term  $\phi^{(1)}(1,2)$  introduced to account for the distortion of the valence electron

$$\psi(1,2) = \phi_0(2) + \phi^{(1)}(1,2) \quad 4.30$$

$$\text{where } \phi_0(2) = R_{1s}(r_2) Y_{00}(\hat{r}_2) \quad 4.31$$

$\phi^{(1)}$  has been determined according to stationary perturbation theory by Reeh (1960). There is a certain ambiguity in the choice of  $\phi^{(1)}$  resolved by choosing it to be orthogonal to the unperturbed wave function.

$$\int \phi_0^*(2) \phi^{(1)}(1,2) d\Omega_2 = 0 \quad 4.32$$

Perturbation theory requires that  $\phi^{(1)}$  satisfies the first order equation

$$(H_{02} - E_0) \phi^{(1)}(1,2) = \left[ \left\{ \int |\phi_0(2)|^2 V d\Omega_2 \right\} - V \right] \phi_0(2) \quad 4.33$$

The interaction potential can be expressed in terms of a complete set of Legendre polynomials and corresponding angular independent functions

$$V \equiv 1/r_{12} - 1/r_1 = \left\{ \sum_{s=0}^{\infty} \gamma_s(r_1, r_2) P_s(\cos \theta_{12}) \right\} - 1/r_1 \quad 4.34$$

$$\text{where } \gamma_s(r_1, r_2) = r_2^s / r_1^{s+1} ; \quad \theta_{12} = \cos^{-1}(\hat{r}_1 \cdot \hat{r}_2) \quad 4.35$$

$r_2$  and  $r_1$  being the lesser and greater of  $r_1$  and  $r_2$ . This prompts the assumption of a similar form for  $\phi^{(1)}$ .

$$\phi^{(1)} = \sum_{s=0}^{\infty} C \tilde{\chi}(r_1, r_2) P_s(\cos \theta_{12}) \quad 4.36$$

$$\text{where } C = 2/\sqrt{\pi}$$

Substitution of these expansions into the perturbation equation provides, by projection onto  $P_s(\cos \theta_{12})$ , a set of equations associated with the relative orbital angular momentum of electrons one and two, having a value  $s\hbar$ .

$$\text{if } s \neq 0. \quad (1/r_2 d^2/d\Omega_1^2 - s(s+1)/r_2^2 + 2/r_2 - 1) \tilde{\chi}_s(1,2) = \gamma_s(1,2) e^{-r_2} \quad 4.37$$

$$\text{if } s = 0. \quad (1/r_2 d^2/d\Omega_1^2 - 2/r_2 - 1) \tilde{\chi}_0(1,2) = -\{ \Gamma(1) - \gamma_0(1,2) \} e^{-r_2}$$

$$\text{where } \Gamma(1) = \int \phi_0(2) \gamma_0(1,2) \phi_0(2) d\Omega_2 = 1/r_1 - e^{-2r_1} (1 + 1/r_1)$$

It will suffice here to make some comments on the solutions of eq.27. A fuller account is contained in appendix (2). The general solution takes a form depending on the relative magnitudes of  $r_1$  and  $r_2$

$$\tilde{\chi}(r_1 > r_2) = y_< + \alpha(r_1) [h_1(r_2) - h_2(r_2)] \quad 4.38$$

$$\tilde{\chi}(r_1 < r_2) = y_> + \beta(r_1) \cdot h_1(r_2)$$

The solutions are chosen to satisfy the physical conditions of finiteness both asymptotically and at the origin. The two solutions are matched at their common boundary  $r_1 = r_2$ , so that both the function and its derivative are continuous. If  $s \neq 0$ ,  $y$  has the general form

$$y = g(r_2) e^{-r_2} r_2^s / r_2^{s+1} \quad 4.39$$

where  $g(2)$  is a linear function of  $r_2$ ,  $h_1$  is an exponentially decaying function of  $r_2$  whose leading term goes like  $1/r_2^{s+1}$  at the origin.  $h_2$  is an exponentially increasing function of  $r_2$ , so chosen that the leading term of  $(h_1 - h_2)$  goes as  $r_2^s$  at the origin. If  $s = 0$ ,  $h_2$  is zero and  $h_1 = e^{-r_2}$ . For  $s = 0$ ,  $y_<$  has a leading term which goes as  $1/r_1$ , for small  $r_1$  and has an exponential decay asymptotically.  $y_>$  has a leading term which goes as  $1/r_2$  and decays exponentially for large  $r_2$ .

Generally  $\alpha$  is a function of  $r_1$ , decaying asymptotically fast enough to kill the asymptotic behaviour of  $h_2$ . Its leading terms goes as  $1/r_1^{s+1}$  at the origin.  $\beta$  is the sum of  $\alpha$  and a function of  $r_1$  chosen to make  $\beta$  go as  $r_1^s$  at the origin. For  $s = 0$ ,  $\beta \rightarrow 1/4 + O(r_1)$ , for small  $r_1$ .

Let us consider the form of the potential terms  $\tilde{V}(1)$ ,  $V_{pol}(1)$  and  $V_d(1)$  defined in eq. 7,13,14 and used in reference to eq.21.

$\tilde{V}(1)$  is the first order interaction potential

$$\tilde{V}(1) \equiv \int \phi_0(2) \cdot V \cdot \phi_0(2) d\underline{r}_2 = -e^{-2r_1} (1 + 1/r_1) \quad 4.50$$

For small  $r_1$ , it goes as  $(-1/r_1 + 1 + O(r_1^2))$ .

Vpol and Vd are both second order interactions depending on the first order perturbed orbital. It will be convenient to express them in terms of the Reeh expansion by substituting from eq.35 and 36.

In Reeh's expansion  $\tilde{\chi}_0$  was chosen to be orthogonal to  $\phi_0(2)$ . This is not consistent with projection operator treatment which leads to the definition of Vd. The conflict can be resolved by a redefinition

$$\tilde{\chi}_0(1,2) = \tilde{\chi}_0^{(REEH)}(1,2) - 2 \sum_{s=0}^{\infty} |\tilde{\chi}_s(1,2)|^2 r_2^2 dr_2 / (2s+1) \quad 4.51$$

a form consistent with the normalisation condition of eq.9. This correction leads to third and higher order terms, which are ignored. In any case from the nature of the terms it is expected that their contribution would be small.

Vpol is the interaction arising from the distorted part of the atomic wave function and the interelectronic interaction potentials. Substituting the expansions of eq.35 and 36 for these quantities Vpol is expressed as an infinite sum of radial functions

$$V_{pol}(r_1) = \int \phi_0(2) \cdot 1/r_{12} \phi^{(1)}(1,2) d\mathbf{r}_2 = \sum_{s=0}^{\infty} V_{pol}^{(s)}(r_1) \quad 4.52$$

$$\text{where } V_{pol}^{(s)}(r_1) = 4/(2s+1) \cdot \int R_{1s}(r_2) \delta_s(r_1, r_2) \tilde{\chi}_s(r_1, r_2) r_2^2 dr_2 \quad 4.53$$

A quantitative comparison of the components of the summation is given in fig. 4.1. Asymptotically, the monopole term of the first order perturbed orbital decays exponentially giving a similar behaviour to the monopole polarization potential whilst dipole and higher order orbitals fall off as  $1/r_1^{s+1}$ . This gives rise to a  $1/r_1^{(2s+2)}$  dependance, for large  $r_1$ , in the corresponding polarization potential with  $s > 0$ . The monopole term is dominant in the intermediate regions and is non-zero at the origin. For small  $r_1$ ,  $V_{pol}^{(0)} \rightarrow -1/2 - 2r_1^2$  whereas  $V_{pol}^{(1)} \rightarrow -2r_1^3/3$ ;  $V_{pol}^{(2)} \rightarrow -16r_1^5/63$  and higher order terms go at least as a fourth power of  $r_1$ .

A study of the polarization potentials arising from third order

interactions, by Dalgarno and Lynn (1957), has indicated that the asymptotic behaviour is dominated by terms which go as the inverse seventh power of  $r$ . This being the case it is not very meaningful to retain terms of second order which fall off more rapidly. For this reason polarization terms up to the quadrupole ( $s = 2$ ) potential will be kept. This latter term is not significant in comparison with the dipole term in any region. Though decaying exponentially in the asymptotic region, where phase shifts <sup>are</sup> most sensitive, the dominant behaviour of the monopole term in the inner region justifies its investigation.

The dynamic potential  $V_d$  arises from the action of the Laplacian operator  $\nabla^2$  on terms quadratic in the first order perturbed orbital. Substitution of the expansion (eq.36) of the latter gives an infinite sum

$$V_d(r) \equiv \int |\nabla \phi^{(1)}(1,2)|^2 d\mathbf{r}_2 = \sum_{s=0}^{\infty} V_d^{(s)}(r) \quad 4.55$$

$$\text{where } V_d^{(s)}(r) = -16/(2s+1) \cdot \int \{ [d\tilde{\chi}_s/d\mathbf{r}]^2 + s(s+1)/r^2 [\tilde{\chi}_s]^2 \} r^2 dr \quad 4.56$$

The asymptotic behaviour of the monopole term is exponential whilst that of higher terms has an inverse  $(2s + 4)$ th power behaviour. For reasons explained above, terms higher than inverse sixth power are ignored. This restriction rejects all terms with  $s > 1$ . Near the origin the monopole term goes as  $r^2$ . The dipole term tends to a finite limit  $V_d^{(1)} \rightarrow -1 + 4r^2$ . It is interesting to note how this term cancels the monopole polarization potential. At the origin this cancellation is exact, giving an  $r^2$  dependence to the combination of polarization and dynamic potentials.

### 3. Numerical Methods

The uncoupled integro-differential equations (eq.20) can be solved by a non-iterative method devised by Percival and reported by Marriott (1958). The equations can be written such that the indefinite integral terms depend on a knowledge of the solution, only for the range from the origin to the

point of consideration. There are also definite integrals requiring the full range of the solution. A transformation gives two integro-differential equations independent of the definite integrals. These equations are solved outward from the origin and used to calculate the transformation factor

Writing the direct term differential operator as

$$D_1 \equiv \left[ \frac{d^2}{dr^2} + k^2 - 1(1+1)/r^2 + 2V_{pol}(r) - 2\tilde{V}(r) + V_d(r) \right] \quad 4.60$$

eq.20 can be expressed as

$$D_1 u_1(r) = C_1 [\rho_1 h_1(r) + F_1(r)] \quad 4.61$$

where  $F(u_1) \equiv F_1(r) = 2 [g_{1,1}^{(1)}(r) h_{-1}(r) + g_{-1}^{(1)}(r) h_{1,1}(r)] \quad 4.62$

and  $g_1^{(1)}(r) = \int_0^r R(t) t^1 u_1(t) dt \quad 4.63$

$$h_1(r) = r^1 R(r) \quad 4.64$$

$$\rho_1 \equiv \rho(u_1(r)) = \delta_{10} \cdot (E_0 - k^2) g_1^{(1)}(\infty) + 2g_{-1}^{(1)}(\infty) \quad 4.65$$

$$C_1 = \pm 1/(2l+1)$$

The substitution  $u_1(r) = Q_1^{(1)}(r) + \mu Q_2^{(1)}(r)$  gives rise to two equations

$$D_1 Q_i^{(1)}(r) = F(Q_i^{(1)}) + \epsilon_i h_1(r) ; \text{ where } \epsilon_1=1 \text{ and } \epsilon_2=0 \quad (4.66)$$

such that  $\mu = -\rho(Q_1^{(1)}) / (\rho(Q_2^{(1)}) - 1) \quad 4.67$

Eq.66 can be solved without a knowledge of  $Q_i^{(1)}$  beyond the considered point in the range of  $r$ . The integration technique adopted is due to Fox and Goodwin (1949). They consider the second order differential equation

$$y'' = fy + g \quad 4.68$$

and show that a combined predictor and corrector for forward integration is

$$(1 - h^2 f_{i+1}/12) y_{i+1} = (2 + 10h^2 f_i/12) y_i - (1 - h^2 f_{i-1}/12) y_{i-1} + h^2/12 (g_{i+1} + 10g_i + g_{i-1}) + C y_i \quad 4.69$$

with a sixth order error term

$$C = -\delta^6/240 + 13/15120 \cdot \delta^8$$

where the variables  $g_i$  and  $f_i$  are functions of  $r_i$  and  $h (= r_i - r_{i-1})$  is the interval.  $g_i$  will contain the integral terms of eq.66. The definite integrals (eq.63) are evaluated by a power series expansion for  $r < 6h$ .

The integrals can then be determined in terms of  $U_j$  (for  $j > i+1$ ) by a Newton-Cotes formula of the open type (Abramowitch and Stegun (1965.)

$$\int_{r_i}^{r_{i+6}} g(r) dr = C_3 \pi h [11g_{i+1} - 14g_{i+2} + 26g_{i+3} - 14g_{i+4} + 11g_{i+5}] \quad 4.70$$



The equation is solved subject to the boundary conditions:

$$\text{At the origin } \mu_1 \xrightarrow{r \rightarrow 0} r^{l+1} (a_{l0} + a_{l1} r + \dots) \quad 4.71$$

The other solution at the origin is divergent and hence unsatisfactory.

$$\text{Asymptotically } \mu_1(r) \xrightarrow{r \rightarrow \infty} A \cdot k^{-1/2} \sin(kr - l\pi/2 + \gamma_1) \quad 4.72$$

where  $\gamma_1$  is the phase shift.

Starting values of the solution near the origin are required by the Fox-Goodwin method. They are determined by assuming a series form for the solution consistent with the boundary conditions at the origin.

$$\mu_1(r) = r^{l+1} \sum_{s=0}^{\infty} a_s r^s$$

Substituting into the indefinite integrals gives

$$g_{l+1}^l(r) \xrightarrow{r \rightarrow 0} 2r^{l+3} [a_0 / (2l+3) + (a_1 - a_0)r / (2l+4) + \dots] \quad 4.74$$

$$\text{and } g_{l-2}^l(r) \xrightarrow{r \rightarrow 0} 2r^2 [a_0 / 2 + (a_1 - a_0)r / 3 + \dots] \quad 4.75$$

$$\text{Thus } F_1 \xrightarrow{r \rightarrow 0} 8r^{l+3} [- (2l+1)a_0 / 2 / (2l+3) + (2l+1)(-a_1 + (5l+9)a_0)r / (l+2) / (2l+3) / 6] \quad 4.76$$

The potential behaves as  $V \rightarrow -1/r + K + O(r^2)$  for small  $r$ .  $K$  is a constant which depends on the form of the approximation considered. The power series ((74) - (76)) are substituted into (66). The first four terms of the series give an accuracy in line with the error inherent in the Fox-Goodwin procedure. (A check built into the programme insists that a comparison between the series and FG solutions should agree to within some previously chosen factor at the point  $r = 6h$ ). The series coefficients are

$$\begin{aligned} a_0 &= 1 \quad \text{chosen arbitrarily} & 4.77 \\ a_1 &= -a_0 / (2l+1) \\ a_2 &= [2C_l \epsilon_l - 2a_1 - (k^2 - \kappa) a_0] / (4l+6) \\ a_3 &= -[2C_l \epsilon_l + 2a_2 + (k^2 - \kappa) a_1] / (6l+12) \end{aligned}$$

Higher power coefficients require a knowledge of the  $r^2$  terms of the potentials. Contributions to  $K$  come from

$$\begin{aligned} 2V_{pol}^{(0)} &\rightarrow -1 + O(r^2) \\ V_d^{(1)} &\rightarrow -1 + O(r^2) \end{aligned} \quad 4.78$$

The first order potential  $2\tilde{V} \rightarrow -2/r + 2$

Hence  $k = 2$

since  $(-2 V_{pol} + V_d) \xrightarrow{r \rightarrow 0} 0$ .

#### 4) Determination of Phase Shifts

The determination of amplitudes and phase shifts follows the method of Burgess (1963) and Seaton and Peach (1962). The method considers solutions calculated to some convenient large, though not asymptotic, value of  $r$ . (here  $r_c = 40$  a.u.). At sufficiently large  $r$  the integro-differential equation (eq.66) becomes

$$\left[ \frac{d^2}{dr^2} - l(l+1)/r^2 - u_3(r) + k^2 \right] u_1(r) = 0 \quad 4.80$$

where the potential  $u_3$  satisfies  $u_3(r)r^3 \xrightarrow{r \rightarrow \infty} 0$ . The integral terms do not contribute as they are modified by an exponentially decaying factor. (Burgess deals with the more general case including a nett charge).

We define the phase shifts and amplitude by imposing the asymptotic condition

$$u_1(r) \underset{r \rightarrow \infty}{\sim} A k^{-1/2} \sin(kr - l\pi/2 + \delta_l) \quad 4.81$$

subject to  $k$  being greater than zero. This form may, in principle, be used to determine both  $A$  and  $\delta$ . In practice the value of  $r$  for which sufficient accuracy is obtainable using eq.81 is prohibitively large.

$$\text{Writing } \omega = k^2 - l(l+1)/r^2 - u_3(r) \quad 4.82$$

we define  $\xi$  by requiring that

$$u_1(r) \sim \xi^{-1/2} \sin(\vartheta(r) + \delta_l) \quad 4.83$$

$$\text{where } \vartheta(r) = \int_a^r \xi(r) dr$$

the lower limit of integration being chosen to satisfy the asymptotic condition of eq.81. Substituting into eq.80 we establish the relationship

$$\xi^2 = \omega + \xi^{1/2} \frac{d^2}{dr^2} \xi^{-1/2} \quad 4.84$$

Assuming that we are considering a region in which the final term on the

right hand side is very much smaller than  $\omega$ , we can solve eq.84 iteratively by choosing  $\xi = \omega^{1/2}$  as a first solution. Adequate accuracy is found with one iteration. Comparison of the solution of eq.66 with eq.83. at nearby points gives the amplitude. Two such points  $r_1$  and  $r_2$  give

$$\alpha_1 = \xi_1^{1/2} \mu_1(r_1) \quad \alpha_2 = \xi_2^{1/2} \mu_1(r_2) \quad 4.85$$

$$\text{then } A = 1/2 [ (\alpha_1 + \alpha_2) \sec^2 \vartheta_{12} + (\alpha_1 - \alpha_2) \operatorname{cosec}^2 \vartheta_{12} ] \quad 4.86$$

where  $\vartheta_{12} = 1/2 \int_{r_1}^{r_2} \xi(r) dr$  is obtained in numerical form.

A is determined at a succession of points until some convergence condition is satisfied.

The calculation of phase shifts is not quite so simple. As it is determined modulo  $\pi$ , a far greater accuracy is required.

Firstly consider the simple case of  $u_3(r) = 0$ . Then

$$\vartheta_0(r) = \int_a^r \xi_0(r) dr \quad 4.87$$

$$\text{where } \xi_0(r) = \omega_0 = k^2 - c/r \quad \text{with } c = l(l+1) \quad 4.88$$

The full solution can be reached with the addition of a numerically determined integral so that

$$\vartheta(r) = \vartheta_0(r) + \int_r^\infty \{ \xi_0 - \xi \} dr \quad 4.89$$

In practice a higher order analytic solution is required. The first iteration of eq.84 gives

$$\begin{aligned} \xi_1 &= (\omega_0 + \omega_0^{1/4} d^2/dr^2 \omega_0^{-1/4})^{1/2} \\ &\approx \omega_0^{1/2} + 1/2 \omega_0^{-1/4} d^2/dr^2 \omega_0^{-1/4} \end{aligned} \quad 4.90$$

The terms neglected make a contribution of order  $r^{-8}$ . Such terms are not significant compared with terms so far neglected from higher orders of iteration, of order  $r^{-6}$ . Using  $\xi_1$ , as the integrand we can determine the corresponding  $\vartheta_1$ . Integrating by parts

$$\vartheta_1(r) = \int_a^r \omega_0^{1/2} dr + 1/2 \omega_0^{-1/4} d/dr \omega_0^{-1/4} \Big|_r^a - 1/2 \int_a^r (d/dr \omega_0^{-1/4})^2 dr = I_1 + I_2 + I_3$$

we can determine each part analytically subject to the conditions that

$$\vartheta_1 \underset{r \rightarrow \infty}{\sim} kr - l\pi/2 \quad 4.92$$

The solutions are

$$I_1 = -\sqrt{c} \cdot \cos^{-1} [\sqrt{c}/kr] + \chi(r) \Big|_r^a \quad 4.93$$

where  $\chi(r) = (k^2 r^2 - c)^{1/2}$

$$I_2 = -c/4 \cdot \chi^{-3} \Big|_r^a$$

$$I_3 = -1/24 [-c \chi^{-3} + 3 \chi^{-1}] \Big|_r^a - 1/(8\sqrt{c}) \cdot \cos^{-1} [\sqrt{c}/(kr)] \Big|_r^a$$

By imposing eq.92 we have

$$\vartheta_1 = [c + 1/8] / \sqrt{c} \cdot \sin^{-1} [\sqrt{c}/(kr)] + \chi - 5c \chi^{-3}/24 - \chi^{-1}/8 - l\pi/2 \quad 4.94$$

$$\text{If } l=0 \quad \text{then } d\omega_0/dr = 0 \quad 4.95$$

$$\text{and } \vartheta_1 = kr \quad 4.96$$

For the case where  $u_3 \neq 0$  we have with  $\vartheta_1$  defined above

$$\vartheta = \vartheta_1 + \int_r^\infty (\xi_1 - \xi) dr \quad 4.97$$

where  $\xi_1$  is given by eq.90 and  $\xi$  by eq.84. Usually the integrand converges rapidly and the integral is easily evaluated numerically. Being of high order in inverse powers of  $r$ , it normally suffices to approximate the integral by

$$\int_r^\infty (\xi_1 - \xi) dr \approx 1/2 \int_r^\infty u_3(r) / \omega_0^{1/2} \cdot dr \quad 4.98$$

In general  $\vartheta_1$  is correct up to order  $r^{-5}$ . Therefore it is important to include  $u_3(r)$  in cases where

$$u_3(r) = \alpha/r^4 + u_4(r) \quad \text{and} \quad u_4(r) \cdot r^4 \xrightarrow{r \rightarrow \infty} 0 \quad 4.99$$

Then the approximation to eq.98 leads to an analytic solution

$$\vartheta = \vartheta_1 + 1/2 \Phi + 1/2 \int_r^\infty u_4(r) / \omega_0^{1/2} \cdot dr \quad 4.100$$

where  $\Phi = -\alpha \chi / (2cr^3) + \alpha k^2 / (2c\sqrt{c}) \cdot \sin^{-1} [\sqrt{c}/(kr)]$  ; if  $l \neq 0$

and  $\Phi = \alpha / (3kr^3)$  ; if  $l=0$

Having consistently neglected terms of order  $r^{-5}$  and kept terms of

lower order, we have up to order  $r^{-4}$  from eq.94 and 100

$$\text{if } l \neq 0 ; \quad \vartheta = \chi [1 - \alpha / (2cr^3) - 1/(8\chi^2) - 5c/(24\chi^3)] - l\pi/2 ; \quad 4.103$$

$$\text{if } l=0 ; \quad \vartheta = kr + \alpha / (3kr^3) \quad 4.104$$

## CHAPTER 5.

### MONOPOLE SUPPRESSION

#### 1. The Semi-empirical Approach to Positron - Hydrogen Scattering

The philosophy behind the Drachman approach (1965) to low energy positron hydrogen scattering is to seek the exact second order potential and then to investigate the effect of modifications. The  $e^+ - H$  system provides a simple model. Not only does it provide known interactions but also avoids symmetry complications. Furthermore below the positronium threshold ( $E < \frac{1}{2}$  ryd) the solution concerns only a single channel.

The procedure is to take a trial wave function based on the hydrogen bound state wave function  $\phi_0$  whilst introducing distortion with the operator  $G(1,2)$ .

$$\Psi = (1 + G(1,2)) \phi_0(2) F(1) \quad 5.1$$

Application of the variational principle to the single particle projectile function whilst neglecting 'velocity terms' due to the action of the kinetic operator on  $G$  gives

$$[-\nabla_1^2 + k^2 + V_1 + V_2] F(1) = 0 \quad 5.2$$

where  $V_1 = \int \phi_0(2) \cdot V \cdot \phi_0(2) d\mathbf{r}_2$  and  $V_2 = \int \phi_0(2) \cdot V \cdot G(1,2) \phi_0(2) d\mathbf{r}_2$ ;  $V_1$  is equal and opposite the first order interaction potential provided by electron-hydrogen scattering.  $V_2$  has been given exactly by Dalgarno and Lynn (1957). The excessive attraction of this potential, indicated by comparison of scattering lengths from the solution of eq.2 ( $a_0 = -2.54$ ) with the variational value of Schwartz (1961) ( $a_s = -2.1$ ), points to the importance of non-adiabatic effects even at low energies.

An alternative evaluation of  $V_2$  is provided using a Legendre polynomial expansion of  $G$

$$G(1,2) = \sum_m G_m(r_1, r_2) P_m(F_{12}) \quad 5.4$$

The monopole term though decaying exponentially is responsible for most of

the short range correlation. The corresponding second order potential is

$$V_{02} = \int \mathcal{D}_0(z) \cdot V \cdot \mathcal{G}_0(1,2) \mathcal{D}_0(z) d\mathbf{r}_1 \quad 5.5$$

The failure of the full adiabatic potential lies in its neglect of the motion of the projectile in the atom.  $V_{02}$  can modify this region by replacing  $V_2$  by  $(V_2 + (\alpha - 1) V_{02})$ . Drachman repeated phase shift calculations for several values of  $\alpha$ . Close agreement with the results of Schwartz is obtained with  $\alpha = 0.1$ , almost full monopole suppression (see Fig. 5.1).

## 2. Determination of the Monopole Suppression Factor by Appeal to $e^-$ - H Bound States.

In the positron hydrogen scattering process the failure of the adiabatic theory to make allowance for velocity dependent terms is shown to be corrected by partial suppression of the monopole term of the polarization potential sum. This leads to excellent values of s-wave phase shifts.

If the method of polarized orbitals is to be extended to more complicated systems difficulties will arise in determining the second order interaction potentials. This applies particularly to the distortion potential introduced by Callaway et al (1966), and depending quadratically on the first order perturbed orbital. It is the purpose of this section to investigate in electron-hydrogen scattering the possibility of avoiding explicit inclusion of these velocity dependent terms by recourse to a simpler approximation. Bearing in mind the success of monopole suppression applied to positron scattering a satisfactory result might be expected here also. Unlike the positron hydrogen system here we have the advantage of known bound states. This knowledge can be used to provide a monopole suppression factor. To this end we shall consider the negative hydrogen ion as the limiting case of the low energy scattering process. This is justified by the small value of the

binding energy of the bound system. In the creation of the  $H^-$  ion model a linear parameter  $\lambda$  is introduced to suppress the contribution of the monopole term of the first order perturbed orbital. The value of the suppression factor might be determined by either a variational treatment or by choosing a value of  $\lambda$  which fits the bound state energy to a previously chosen value, say the variationally derived value of Pekeris (1958).

We shall consider the model of the  $H^-$  system to be composed of an electron, the original atomic electron, described by an adiabatically distorted ground state wave function whilst the other electron, initially incident, is represented by an unperturbed ground state wave function.

In a simpler model consider the incident electron introduced into the hydrogen atom such that both electrons occupy ground state (1s) orbitals without requiring allowance for mutual distortion effects in the wave functions. The Pauli principle insists that only the singlet case be valid. The trial wave function is

$$\Psi(1,2) = \frac{1}{\sqrt{2}} (1 + P_{12}) \phi_0(1) \phi_0(2) \quad 5.10$$

so that the total energy of the bound state system becomes

$$E = \int \Psi (H_{02} + H_{01} + V) \Psi d\tau_1 d\tau_2 = 2E_0 + \bar{V} \quad 5.11$$

$$\text{where } \bar{V} = \langle \phi_0(1) \phi_0(2) | \frac{1}{r_{12}} | \phi_0(1) \phi_0(2) \rangle \quad 5.12$$

This gives a value of  $E = -\frac{3}{4}$  ryd, or a negative electron affinity for the atom of 0.25 ryd. The electron affinity is the difference between the bound state energy and that of the systems comprising the hydrogen atom plus free electron of zero incident energy. The variationally derived value of Pekeris gives the electron affinity as positive and equal to 0.0555 ryd.

The distortion in the wave function of the hydrogen atom is chosen in first order perturbation theory. Using the Reeh expansion (eq.4.36) the first order perturbed orbital is written in terms of the complete set of

Legendre polynomials. A linear suppression factor is applied to the monopole term. The second electron function remains undistorted. The trial function is

$$\Psi(1,2) = \frac{1}{\sqrt{2}} (1 + P_{12}) [\phi_0(2) + \chi_\lambda(1,2)] \phi_0(1) \quad 5.13$$

where

$$\chi_\lambda(1,2) = \lambda \chi_0(1,2) + \sum_{s>0} \chi_s(r_1, r_2) P_s(r_{12}) \quad 5.14$$

(see eq.4.36). It can be shown, using the notation of eq.4.34 and 4.50, that

$$(H_{02} - E_0) \chi_\lambda(1,2) = [\lambda (\tilde{V}(1) - V_0) - (V - V_0)] \phi_0(2) \quad 5.15$$

where  $\tilde{V}$  is the averaged central field interaction potential and  $V_0$  the monopole term of a Legendre polynomial expansion of  $V$ .

We require the value of  $E$  up to second order in interaction terms, where

$$E = \left[ \int \Psi H \Psi d\underline{r}_1 d\underline{r}_2 \right] / \left[ \int |\Psi|^2 d\underline{r}_1 d\underline{r}_2 \right] \quad 5.16$$

All terms arising from the action of the Laplacian operator on the first order perturbed orbital are neglected along with third and higher order interactions. The former terms are equivalent to the distortion potentials which are superseded by monopole suppressions. Similar terms were neglected in the previous work of Drachman.

Substituting from eq.13 and 14, eq.16 gives ( in a.u.)

$$E = \left[ -3/8 + \lambda/2 (4 - \lambda) K_0 + \frac{3}{2} \sum_{s>0} K_s + \lambda^2 L_0 + \sum_{s>0} L_s \right] / \left[ 1 + \lambda^2 M_0 + \sum_{s>0} M_s \right] \quad 5.17$$

where

$$K_s = \int |\phi_0(1)|^2 \phi_0(2) \frac{1}{r_{12}} \chi^{(s)}(1,2) d\underline{r}_1 d\underline{r}_2$$

$$L_s = 8/(2s+1) \left[ \int |\phi_0(1)|^2 (r_1^{-1}) |\chi_s(1,2)|^2 d\underline{r}_1 d\underline{r}_2 + \left\{ \int \phi_0(1) (r_1^{-1}) \chi_s(1,2) \chi_s(2,1) \phi_0(2) d\underline{r}_1 d\underline{r}_2 \right\} \right]$$

$$M_s = 8/(2s+1) \left[ \int |\phi_0(1)|^2 |\chi_s(1,2)|^2 d\underline{r}_1 d\underline{r}_2 + \left\{ \int \phi_0(1) \chi_s(1,2) \chi_s(2,1) \phi_0(2) d\underline{r}_1 d\underline{r}_2 \right\} \right]$$

A table of  $K$ ,  $L$  and  $M$  is given below.

Keeping all terms up to second order provides a minimum value, for variation with respect to  $\lambda$ , at  $\lambda = 1/3$ . The associated bound state energy of the system is  $E = -0.97$  ryd, a negative electron affinity of 0.03 ryd. No bound is formed. However, retaining only linear  $\lambda$  dependent terms a fit to



the Pekeris value can be found

$$E(\lambda) = [-0.375 + 2\lambda K_0 + 3/2 \sum_{s>0} K_s + \sum_{s>0} L_s] / [1 + \sum_{s>0} M_s] = -0.528 \text{ a.u.}$$

giving  $\lambda = 0.35$

If all terms above first order of interaction are ignored the fit

$$E(\lambda) = [-0.375 + 2\lambda K_0 + 3/2 \sum_{s>0} K_s] = -0.528 \text{ a.u.}$$

provides  $\lambda = 0.28$ .

S	Ks (ryd)	Ls (ryd)	Ms (ryd)
0	-0.1784	0.1840	0.2006
1	-0.1202	-0.0272	0.1600
2	-0.0170	-0.0024	0.0100
$\sum_{s>0}$	-0.1372	-0.0296	0.1700

The table gives the values of the components of eq.17. The positive value of  $L_0$  is consistent with the fact that the monopole term concentrates its effect on the small  $r$  values of  $(1-r)$ .

### 3. $e^-$ - H Scattering with Monopole Suppression

A phase shift comparison between the monopole suppression (ms), Exchange adiabatic total (AET), exchange adiabatic dipole (AED) (no monopole, or quadrupole), and the extended polarization (EP) approximations are shown in fig 4.3 to 4.5.

Whilst all the M.S. phase shifts tend to the EP at low energies, where they are insensitive to variations of the monopole suppression factor  $\lambda$ , only the triplet s-wave values remain in agreement as the energy increases. These latter values are seen to be least sensitive to the inclusion of polarization. In all cases the MS values lie above the E.P values, There is general agreement in shape, the exceptions being the singlet p-wave phase shifts which remains positive in the M.S approximation. The closest agreement with the E.P approximation is always provided by complete monopole suppression.

The difference between M.S and AED results indicates that the quadrupole

polarization potential moves the phase shifts away from the E.P. approximation. This is particularly apparent as higher partial waves are considered.

The linear behaviour of the plot of s-wave singlet and triplet phase shift against the monopole suppression factor demonstrates that any choice of the suppression factor would lead to a value lying between the M.S and AED curves (fig. 5.3).

## CHAPTER 6.

INELASTIC CROSS SECTIONS

To indicate the origin of the effects of distortion the full second order effects on cross sections will be included in several stages.

Consider the transition matrix:

$$T_{ij} = \langle \psi_i | V | \psi_j^+ \rangle \quad 6.1$$

where  $\psi_i^+$  is the trial wave function of the system for the particular approximation under consideration and  $\psi$  is the exit channel wave function.

We shall consider the following approximations.

1)  $\psi$  is taken to include distortion in the atomic wave function only. The incident particle is described by a plane wave function as in the symmetrized Born approximation. This is described as the polarized Born approximation but includes the usual exchange terms. If no attempt is made to guarantee the orthogonality of the initial and final states the resulting cross sections vastly exceed those of the Born approximation.

2) Rather than include the distortion in the atomic wave function its effects can be taken into account through the variational single particle function describing the projectile. The atomic wave function contributes in an equivalent way to its role in the symmetrized Born approximation. By neglecting the distortion in the projectile wave function but keeping exchange the approximation provides the fully symmetrized exchange approximation.

3) The distortive effect of (1) and (2) can be brought together. Though only direct distortion terms will contribute to the projectile function distortion, we include either direct only or direct plus exchange terms in the atomic wave function.

The initial wave function will be considered in the most general form

$$\Psi_i^+(1, 2) = (1 \pm \rho_{12}) [\phi_0(2) + \phi^{(1)}(1, 2)] F(1) \quad 6.2$$

where F includes all effects of the extended polarization approximation,

The transition matrix is given by

$$T_{if}^{\pm} = 1/(2\pi) \cdot \langle \phi_i(2) \cdot \exp(i \underline{k}_i \cdot \underline{r}_i) | 1/r_{12} - 1/r_1 | (Z_{12} \pm Z_{21}) \rangle \quad 6.3$$

where

$$Z_{12} = Z_{12}^{(0)} + Z_{12}^{(1)} \quad 6.4$$

and

$$Z_{12}^{(0)} = \phi_0(2) \cdot F(1)$$

$$Z_{12}^{(1)} = \phi^{(1)}(1, 2) F(1)$$

#### 1) POLARIZED BORN APPROXIMATION.

As a first approximation eq. 3 and 4 are replaced by symmetrised polarized Born approximation

$$Z_{12} = [\phi_0(2) + \phi^{(1)}(1, 2)] \cdot \exp(i \underline{k}_i \cdot \underline{r}_i) \quad 6.5$$

and

$$T_{if} = 1/2\pi \cdot \langle \phi_i(2) \cdot \exp(i \underline{k}_i \cdot \underline{r}_i) | 1/r_{12} - 1/r_1 | Z_{12} \pm Z_{21} \rangle \quad 6.6$$

For the moment consider only the direct terms constituting the polarized Born approximation. Thus eq. 6 reduces to

$$T_{if} = T_{if}^{(0)} + T_{if}^{(1)} \quad 6.7$$

where  $T_{if}^{(0)}$  is the Born matrix. The right hand term carries the distortion introduced by the incident electron. At low energies a perturbation theory approach should be valid.

$$T_{if}^{(1)} = \langle \psi_f | V | \psi_i^{(1)}(1, 2) \rangle \quad 6.8$$

where  $\psi_i^{(1)}$  is the product of the plane wave projectile function and the first order perturbed orbital, defined in eq. 4.36. in terms of a complete set of

Legendre polynomials and corresponding functions  $\tilde{\chi}_s(1,2)$ , depending on the radial coordinates  $r_1$  and  $r_2$ .  $V$  is the Coulomb potential defined in eq.4.34 in terms of Legendre polynomials and corresponding functions  $\mathcal{Y}_s(r, r_2)$ .

We can write

$$T_{if}^{(a)} = 1/(2\pi) \cdot \int d\underline{r}_2 \exp(i \underline{p} \cdot \underline{r}_2) f(\underline{r}_2) \quad 6.9$$

where

$$f(\underline{r}_2) = \int \mathcal{Y}_i(2) \cdot V(1,2) \cdot \mathcal{Y}^{(a)}(1,2) d\underline{r}_1$$

and 6.10

$$\underline{p} = \underline{k}_i - \underline{k}_f$$

Using the expansions described above for  $V$  and  $\mathcal{Y}^{(a)}$ ,  $f(\underline{r}_2)$  can be shown to reduce to an infinite sum of radial integrals for ground state scattering to the  $n = 2$  level.

### 1s - 2s Scattering

The Born element is written as

$$T_{if}^{(a)} = 2/p \cdot \int_0^\infty \sin(p r_1) \cdot r_1 \left\{ \int_0^\infty R_{2s}(r_2) \mathcal{Y}_0(r_1, r_2) R_{1s}(r_2) r_2' dr_2 \right\} dr_1 \quad 6.11$$

The first order element is given by eq.9 with

$$\begin{aligned} f(r_1) &= -1/r_1 \int \mathcal{Y}_{2s}^*(2) \mathcal{Y}^{(a)}(r_1, r_2) d\underline{r}_2 + \int \mathcal{Y}_{2s}^*(2) \cdot 1/r_{12} \cdot \mathcal{Y}^{(a)}(1,2) d\underline{r}_2 \\ &= 4 \left\{ -1/r_1 \int_0^\infty R_{2s}(r_2) \tilde{\chi}_0(r_1, r_2) r_2' dr_2 + \sum_{s=0}^\infty \int_0^\infty R_{2s}(r_2) \mathcal{Y}_s(r_1, r_2) \tilde{\chi}_s(r_1, r_2) r_2' dr_2 / (2s+1) \right\} \end{aligned} \quad 6.12$$

This expression is seen to consist of functions depending on  $r_1$  and  $r_2$  but not  $\hat{r}_1$  or  $\hat{r}_2$ . Such being the case it follows that

$$T_{if}^{(a)} = 2/p \cdot \int_0^\infty f(r_1) \cdot \sin(p r_1) \cdot r_1 \cdot dr_1 \quad 6.13$$

However with this choice of  $\Psi_i^*$ ,  $\langle \Psi_i | \Psi_i^* \rangle \neq 0$ . In order to

ensure orthogonality we require that

$$\int R_{2s}(r_2) \tilde{\chi}_0(r_1, r_2) \cdot r_2' dr_2 = 0 \quad 6.14$$

resulting in the disappearance of the first term of eq.12.

1s - 2p Scattering

The final state has a different orbital angular momentum state than the initial state

$$\psi_f(\mathbf{r}) = R_{2p}(r) Y_{lm}(\hat{r}) \quad 6.15$$

The Born T-matrix element in terms of the spherical bessel function  $j_1(\rho r)$  is

$$T_{if}^{(0)} = 2i \sqrt{4\pi}/3 \left\{ \int_0^\infty dr_1 r_1^2 j_1(\rho r_1) \int_0^\infty dr_2 r_2^2 R_{2p}(r_2) \delta_l(r_1, r_2) R_{1s}(r_1) \right\} Y_{lm}(\hat{p}). \quad 6.16$$

The first order term gives

$$T_{if}^{(1)} = [I_2 - I_1] / (2\pi) \quad 6.17$$

where

$$I_1 = 8i \sqrt{4\pi}/3 \left\{ \int_0^\infty j_1(\rho r) r^2 dr \cdot \frac{1}{r} \int_0^\infty R_{2p}(r) \tilde{\chi}_l(r, r) r^2 dr \right\} Y_{lm}(\hat{p}) \cdot 2\pi$$

and

$$I_2 = 8i \sqrt{4\pi}/3 \left\{ \int_0^\infty dr_1 r_1^2 j_1(\rho r_1) \int_0^\infty dr_2 r_2^2 R_{2p}(r_2) \delta_l(r_1, r_2) \tilde{\chi}_s(r_1, r_2) \cdot \begin{pmatrix} 1 & s & \lambda \\ 0 & 0 & 0 \end{pmatrix}^2 \right\} Y_{lm}(\hat{p}) \cdot 2\pi$$

$\begin{pmatrix} 1 & s & \lambda \\ 0 & 0 & 0 \end{pmatrix}$  are Wigner 3 - j coefficients (see Messiah II, 1057, eq. C15b and C16). Summing over the final  $m'$  states, the differential cross section is

$$|T_{1s, 2p}|^2 = \sum_{m'} |T_{1s, 2p m'}|^2 = 3 |F(\rho)|^2 \quad 6.18$$

where

$$F(\rho) = \int_0^\infty j_1(\rho r) r^2 f(r) dr$$

and

$$f(r) = \int_0^\infty \left\{ \frac{2}{3} R_{2p}(r_2) \delta_l(r_1, r_2) R_{1s}(r_1) - \frac{8}{3} R_{2p}(r_1) \frac{1}{r_1} \tilde{\chi}_l(r_1, r_2) \right. \\ \left. + 8 \sum_{s, \lambda} \frac{[(s+1)\delta(\lambda, s+1) + s\delta(\lambda, s-1)]}{(2\lambda+1)(2s+1)} R_{2p}(r_2) \delta_\lambda(r_1, r_2) \tilde{\chi}_s(r_1, r_2) \right\} r_2^2 dr_2 \quad 6.19$$

The orthogonality condition

$$\int_0^\infty R_{2p}(r_2) \tilde{\chi}_1(r_1, r_2) r_2^2 dr_2 = 0 \quad 6.20$$

requires that the second term of  $f(r_1)$  vanishes.

Cross sections result by substituting the T-matrix (eq.7 with eq.11,13, 16,18) into eq.0.22 and integrating over momentum transfer.

The <sup>Oppenheimer</sup> polarised Born, direct and direct plus exchange approximation transition amplitudes are respectively written as

$$T_{if}^{(d)} = \frac{1}{2\pi} \langle \phi_f(x) \exp(i \underline{k}_f \underline{r}_1) | V_{r_1} - V_{r_2} | Z_{12} \pm Z_{21}^{(s)} \rangle \quad 6.21$$

and

$$T_{if}^{(de)} = \frac{1}{2\pi} \langle \phi_f(x) \exp(i \underline{k}_f \underline{r}_1) | V_{r_1} - V_{r_2} | Z_{12} \pm Z_{21} \rangle \quad 6.22$$

where

$$Z_{21}^{(s)} = \phi_0(1) \cdot \exp(i \underline{k}_1 \underline{r}_1) \quad 6.23$$

$T_{if}^{(de)}$  will not be evaluated by the above treatment (integrating numerically over momentum transfer) but from a simplification of the full polarization treatment of section 3.

For the 1s-2s and 1s-2p scattering processes total and differential cross sections have been calculated in a series of approximations to the polarized Born approximation (fig.6.1 to 6.4). Due to the series nature of the first order polarized orbital it is possible to isolate the contribution of each of these terms to the scattering amplitude.

As the transition amplitude is an intermediate calculation in the evaluation of total cross sections it is possible to investigate the effect of the alternative Moiseiwitch definition of the differential cross sections. This suggests replacing

$$|T_{if}|^2 = |T_{if}^{(d)} + T_{if}^{(e)}|^2 \quad 6.24$$

the definition used elsewhere in this thesis, by

$$|\overline{T}_{if}|^2 = |\overline{T}_{if}^{(2)}| + |\overline{T}_{if}^{(3)} + 2\overline{T}_{if}^{(1)}| \quad 6.25$$

on the grounds that eq.24 includes additional fourth order terms. In view of the approximations that are necessary elsewhere, it is not clear how a consistent form should be constructed.

For the 1s-2s process the total cross section contribution from terms associated with  $s > 2$  (eq.12) is negligible in the energy range considered. The full polarized Born calculation will be taken to be that with the first three terms. Neglect of the monopole contribution (Total Monopole suppression) causes the approximation to give results in excess of the Born above 1.1 ryd. Neglect of the quadrupole contribution is much less drastic, agreement being very close below 0.95<sup>ryd.</sup> between the full approximation and that retaining  $s = 0$  and  $s = 1$  terms. At the greatest the difference between this approximation and the <sup>full polarized</sup> Born is less than 15% though the approach to the  $FA$  Born is very slow at higher energies. The choice of the Moiseiwitch convention gives rise to only small changes in the total cross section. The greatest difference at 1.2 ryd. is less than 5%. The two forms converge rapidly above this energy.

The 1s-2p total cross section calculations indicate the necessity of including the first four ( $s = 0, 1, 2, 3$ ) partial amplitudes in eq.19. Neglect of the  $s = 3$  contribution causes an increase in the cross section of up to 7%, slightly less than the difference due to using the alternative Moiseiwitch convention. Complete monopole suppression appears to counteract neglect of contributions higher than quadrupole. Though agreement between the full approximation and that retaining only the  $s = 1$  and 2 partial amplitudes is to within a few per cent, this cancellation between neglected terms would seem fortuitous.



The form of the total cross sections is indicated by the structure of the differential cross sections shown at 1.0 ryd. (fig. 6.3 and 6.4). The curves corresponding to the inclusion of different partial amplitudes show general agreement in shape and peak positions for 1s-2p transitions, variations being restricted to the magnitudes. In 1s-2s transitions the different approximations demonstrate shapes which are somewhat out of phase with one another, causing the crossing of the total cross section curves. The large contribution of the Moiseiwitch differential cross sections at small angles seems to be largely compensated for by the dip at intermediate angles (due to the changing sign of  $(T_{if}^{(s)} + 2 \cdot T_{if}^{(v)})$  in eq.25).

## 2) Single Particle Polarization Approximation

Restricting distortion to the projectile wave function is equivalent to replacing the symmetrised Born transition amplitude by

$$T_{if} = \frac{1}{2\pi} \langle D_f(z) \exp(i k_f r_f) | \frac{1}{r_{12}} - \frac{1}{r_1} | Z_{12}^{(o)} \pm Z_{21}^{(o)} \rangle \quad 6.30$$

where  $Z_{12}^{(o)}$  is defined in eq.4.  $F(1)$  can be expanded in terms of reduced radial functions  $u_l^\pm$  associated with the  $l$  th partial wave (eq. 4.16), normalised to the asymptotic form

$$u_l^\pm(r) \sim k^{-1/2} \sin(kr - l\pi/2 + \gamma_l^\pm) \quad 6.31$$

Noting the difference between this normalisation and that for the spherical bessel function (eq.21.15) the evaluation of cross sections follows exactly as for Born cross sections in Chapter 2. Replacing  $f_s(k, r)$  by the reduced radial functions of appropriate symmetry then, from eq.2.27 to 2.32., for the 1s-2s scattering process the cross sections we obtain are

$$Q(1s-2s) = 4k_f/k_i^2 \sum_{s=0}^{\infty} \left\{ |P_s^+(1s-2s)|^2 + 3 |P_s^-(1s-2s)|^2 \right\} (\pi a_0^2) \quad 6.32$$

where

$$P_s^\pm(1s-2s) = \int_0^\infty \mu_s^\pm(r_1) r_1 e^{-r_1/2} (1/2)^{1/2} \cdot \left\{ \pm(2-r_1) [2\delta_{s0}/(1+k_1^2) - J_{k_1}^{(s)}/(2s+1)] - 8/21 \cdot e^{-r_1} j_s(k_1 r_1) (2+3r_1) \right\} dr_1 \quad 6.33$$

For the 1s-2p process the cross section may be expressed as

$$Q(1s-2p) = 4k_1/(3k_1^2) \sum_{s=0}^\infty \left\{ |P_s^+(1s-2p)|^2 + 3|P_s(1s-2p)|^2 \right\} (\pi a_0^2) \quad 6.34$$

where

$$|P_s^\pm(1s-2p)|^2 = [s \cdot H^\pm(s-1, s)^2 + (s+1) H^\pm(s+1, s)^2] / (2s+1) \quad 6.35$$

and

$$H^\pm(s, \lambda) = \int_0^\infty dr_1 r_1 \mu_s^\pm(r_1) (1/2)^{1/2} / \sqrt{3} \cdot \left\{ b_4/(81r_1^2) [8 - e^{-3r_1/2} (8 + 12r_1 + 9r_1^2 + 27r_1^3/4)] j_\lambda(k_1 r_1) \pm r_1 e^{-r_1/2} / (2\lambda+1) [3J_{k_1}^{(\lambda)} - 2\delta_{s1} \delta_{\lambda 0} / (1+k_1^2)] \right\} \quad 6.36$$

$J_{k_1}^{(\lambda)}$  is defined in eq.2.29. A more detailed account of the 1s-2p calculation is given in Appendix 4.

Several approximations follow depending on the choice of projectile wave function. Here we shall consider:

- (1) Exchange approximation - in which F is the symmetrised central field solution. No polarization is included..
- (2) Adiabatic approximation - in which second order direct polarization terms are retained (Labahn and Callaway, 1964).
- (3) Extended polarization - in which the full direct second order interaction terms are kept (Callaway et al, 1968).

In fig. 6.20, 1s-2s cross sections in which the single particle wave function, is described by the central field exchange and the extended polarization approximations are shown in comparison with 3 - state and six-state close coupling values (Burke, Ormonde and Whitaker, 1967), the Born approximation

and experiment (Fite renormalised results of Lichten and Schultz - Chapter 3). At low energies (below 0.8 ryd) the agreement between the two single particle approximation values is almost exact. At this same energy the approximations move very close to the close coupling approximations. This is just the region where the three state and six state <sup>values</sup> most closely agree, and it might be expected that the neglected higher coupled states have least significance. Above this energy the single particle approximations slowly diverge, the exchange approximation falling below almost to touch the experimental curve at its peak whilst the EP curve moves towards the six state values. The single particle approximations are bounded by the six state and experimental curves, above and below respectively, throughout the range of available results. Agreement between the former approximation curves is fairly close throughout the energy range being at most of the order of 8%. Table 6.1 indicates that above 4 ryd. the approximations are slowly converging. The approach to the Born approximation is slow. A difference of the order of 10% shows even at 9 ryd. The peak values of the exchange and EP approximations are 0.19 and 0.195 (  $\pi a_0^2$  ) respectively. Peak positions at 0.825 ryd agree closely with the six-state value, lying just below that of the experimental curve.

The adiabatic cross sections (fig.5.4) demonstrate a considerable change in magnitude compared to the E.P. approximation, though there is general agreement in shape. The peak positions coincide with the E.P. peak whilst the peak value of the AET approximation is about 50%, and those of the AED and MS approximations about 75% of the E.P. peak value. This demonstrates the relative equivalence of the effects of the monopole polarization, and the dynamic distortion potentials which holds up to about 1 ryd.

Above this energy the adiabatic approximations converge rapidly. Convergence to the E.P. approximation is somewhat higher (about 1.5 ryd). The comparison of the AED and MS curves shows that the effect of neglecting the quadrupole potential is never more than a few per cent.

A second peak is apparent in the single particle approximations at about 1.5 ryd (fig.5.4.) The existence of a second peak is indicated by the experimental results of Hils et al (1966) (see fig. 3.1), with a peak maximum at 4.5.ryd. The experimental peak maximum to first minimum difference of 0.007 ( $\pi a_0^2$ ) compares with a difference of 0.02 ( $\pi a_0^2$ ) for the extended polarization approximation (fig.6.24). Compared with other theoretical approximations (fig.5.4) the extended polarization approximation, which would be expected to yield the best results, moves slightly towards agreement with experiment.

The origin of the second peak in the extended polarization approximation 1s-2s total cross sections can be understood from the relative contributions of the singlet and triplet partial cross sections (see table 6.5). The total singlet cross section and suitably weighted triplet D wave partial cross section are shown in fig. 6.25. For singlet cross sections, the S-wave contribution is dominant at low energies ( $k^2 < 1$  ryd) giving way to a dominant P-wave partial cross section above  $k^2 = 2$  ryd. The total effect produces a singlet cross section which falls off from 0.27 ( $\pi a_0^2$ ) at  $k^2 = 1.1$ ryd to 0.12 ( $\pi a_0^2$ ) at  $k^2 = 3$  ryd. In this energy range the triplet cross sections are dominated by the D wave partial cross section, with a maximum value of 0.03 ( $\pi a_0^2$ ) at  $k^2 = 1.8$  ryd. This can be explained by the large triplet D-wave phase shifts above  $k^2 = 1$  ryd (see fig.4.5). Though the singlet cross section dominates over the triplet value in the

single particle and close coupling approximations the similar disparity displayed by the partial cross sections might be expected. However the great disagreement in the relative magnitudes is surprising. For singlet scattering the extended polarisation s-wave value exceeds the close coupling approximation by a factor of more than two at their respective peaks, though the peak positions of the E.P and 6- state approximations agree well. For higher partial waves than  $\ell = 3$ , the contribution to the total cross section in the E.P approximation is negligible in the region of energies covered by the close coupling calculations. This is contrary to the situation which holds in the close coupling approximation, though it should be noted that the E.P results have not achieved their peak values, in this energy range.

Triplet E.P. results give no better agreement with close coupling values though their effect on the total cross section is small, contrary to the case of the triplet p-wave close coupling values. It is interesting to assess the role played by polarization and distortion potentials in the character of the partial cross sections. Comparison between the exchange approximation, which owes nothing to these potentials and the E.P approximation indicates why total cross sections are little influenced by these more inclusive effects. Whilst the triplet partial cross sections,  $S^-$  and  $P^-$ -wave values differ considerably in magnitude, and for the  $S^-$ -wave also in shape, the dominant role of the singlet partial cross sections render these differences negligible. The  $P^-$ -wave cross section is also different in that the exchange values exceed those of the E.P. approximation. The singlet values agree well in both magnitude and shape, particularly so for the dominant s-wave cross sections.

Fig. 6.21 compares 1s-2p cross sections for two single particle

approximations (exchange, and extended polarization) with the 3-state and 6-state close coupling values (Burke, Ormonde and Whitaker-1967) which agree so well with the experimental points of Chamberlain et al (1964), also shown. The close coupling and experimental results are given for perpendicular cross sections. They have been converted to total cross sections using eq.3.3 and the values of the polarization given by Burke, Taylor and Ormonde (1967) (fig.3.5).

Unlike the 1s-2s cross sections the exchange and extended polarization cross sections differ greatly at low energies, the E.P values being as much as 30% lower at 0.85 ryd. The disagreement extends up to about 1 ryd, above which the two curves slowly converge. For energies between 0.77 ryd and the  $n = 2$  threshold resonance region ( $E = 0.87$  ryd), the E.P approximation results show good agreement with the close coupling results. Above 0.825 ryd. the 6-state and 3-state curves diverge. The E.P curve lies between them remaining closer to the more inclusive 6-state values. At very low energies the single particle approximations go to zero, being modified by  $k$ , the final momentum, while experimental values display a finite threshold effect.

The maximum cross section in the E.P approximation is at  $E = 2.5$  ryd, just above that of the Born approximation (tab. 6.2). The peak value is  $1.1 (\pi a_0^2)$  compared with the Born peak of  $1.3 (\pi a_0^2)$ . Convergence to the Born approximation is much faster than in the 1s-2s transition, agreement being to within 5% above 4 ryd.

Comparison of the adiabatic approximations with the E.P approximation is shown in fig. 5.5. The effect of the monopole suppression is negligible on the scale shown and both MS and AET cross sections are represented by one curve. This curve falls well below the E.P curve at low energies

( $E < 0.9$  ryd), where the cross sections of the latter approximation agree so well with close coupling. With increasing energy the exchange adiabatic curve approaches the E.P curve crossing at 1.1 ryd and converging to it slowly at higher energies.

As a result of the different way of approaching partial cross sections for transitions on which the angular momentum of the atomic electron does not remain zero, comparison of close coupling and E.P partial wave cross sections have proved impossible.

In fig. 6.11 to 6.15 1s-2p partial cross sections are given in the central field exchange and extended polarization approximations. The agreement in shape seen between these two approximations in 1s-2s transitions is also observed here but there exists much greater disagreement in magnitude, which is reflected in the total cross sections. The exchange values exceed those of the E.P approximation in all partial cross sections but the triplet s-wave. However as this contribution is down by a factor of a hundred compared with the other contributions its effect is negligible. Difference in the magnitude of both singlet and triplet p-wave partial cross sections is somewhat over-shadowed by the similarity of the characteristics displayed by the singlet s and d-wave contributions.

TABLE 6.1 - 1s - 2s TOTAL CROSS SECTIONS ( $\pi a_0^2$ )

	BORN	EXCH. APP.	EXT. POL.
$k^2 = 0.77$ (ryd.)	0.1095	0.1420	0.1415
0.80	0.1621	0.1822	0.1839
0.825			0.1935
0.85	0.2066	0.1854	0.1927
0.90	0.2295	0.1677	0.1789
1.00	0.2483	0.1294	0.1443
1.10	0.2509	0.1048	0.1194
1.44	0.2280	0.0880	0.1237
2.00	0.1831	0.0990	0.1198
2.25	0.1670		0.0982
3.00	0.1314		
4.00	0.1020	0.0743	0.0792
9.00	0.0477		0.0437



TABLE 6.2 - 1s - 2p TOTAL CROSS SECTIONS. ( $\pi a_0^2$ )

	BORN	EXCH. APP.	EXT. POL.
$k^2 = 0.77$ (ryd)	0.342	0.386	0.237
0.80	0.528	0.507	0.328
0.82	0.617	0.542	0.364
0.85	0.725	0.569	0.406
0.90	0.859	0.597	0.467
1.00	1.038	0.664	0.589
1.10	1.150	0.747	0.703
1.50	1.21		0.975
2.00	1.310		1.068
2.50	1.25		1.105
3.00	1.174		1.076
4.00	1.041		0.988
9.00	0.662		0.634

TABLE 6.3 - 1s - 2s TOTAL CROSS SECTIONS. ( $\pi a_0^2$ )

	B.O.	DIR.	POL. B.O. DIR + EX.	FULL POLARIZATION DIR.	DIR + EX.
$k^2 = 0.77$ (ryd)	1.34	1.145	0.853	0.2261	0.0387
0.80	1.83	1.553	1.070	0.2986	0.260
0.85	2.05	1.710	3.108	0.3178	0.720
0.90	1.98	1.646	4.120	0.2990	1.083
1.00	1.65	1.351	3.879	0.2431	1.086
1.10	1.30	1.053	2.806	0.1951	0.766
1.44	0.60				

contd....

TABLE 6.3 (Cont'd)

	B.O.	DIR.	POL. B.O. DIR + EX.	FULL POLARIZATION DIR.	DIR + EX.
2.25	0.20				
4.00	0.096	0.0878		0.0880	
9.00	0.045	0.0417		0.0420	

TABLE 6.4 - 1s-2p TOTAL CROSS SECTIONS. ( $\pi a_0^2$ )

	B.O.	POL. B.O. DIR.	FULL POLARIZATION DIR.
$k^2 = 0.77$ (ryd)	1.42	0.990	0.156
0.80	1.88	1.292	0.223
0.85	2.01	1.392	0.290
0.90	1.92	1.387	0.346
1.00	1.66	1.018	0.441
1.10	1.46	0.874	0.518
1.44	1.45		
2.25	1.13		
4.00	0.973	0.907	0.904
9.00	0.648	0.638	0.637

## FULL POLARISATION APPROXIMATION

A more inclusive approach to polarization than those met with above is provided by eq. 6.3 whereby all first and second order terms of the scattering amplitude are retained.

In fact it has not proved possible to provide the full second order projectile wave function. Instead we use the extended polarization approximation in which higher order exchange interactions are ignored. It may be better to keep only direct higher order contributions from the distorted atomic wave function. As such the direct and exchange contributions are introduced separately.

The full direct second order contribution to the transition amplitude gives

$$T_{if,d}^{(2)} = \frac{1}{2\pi} \langle \psi_f(z), \exp(ik_f z) | V_{02} - V_1 | Z^{(1)}(1,2) \rangle = \frac{1}{2\pi} [I_3^+ - I_4^+] \quad 6.40$$

where

$$Z^{(1)}(1,2) = F(1) \cdot \psi^{(1)}(1,2) \quad 6.41$$

The importance of having the initial and final states orthogonal was stressed above. This requirement gives  $I_4^+ = 0$ . 6.42

### 1s-2s Scattering

$$I_3^+ = 16\pi \int_{-i}^i \int_0^\infty j_2(k_f r_1) u_1^+(r_1) r_1 dr_1 \int_0^\infty R_{2s}(r_2) \frac{\delta_1(r_1, r_2) \tilde{\chi}_2(r_1, r_2) r_2^2 dr_2}{(2l+1)} \cdot Y_{50}(\hat{k}_f) \quad 6.43$$

$$I_4^+ = 16\pi \int_{-i}^i \int_0^\infty j_2(k_f r_1) u_1^+(r_1) r_1 dr_1 \int_0^\infty R_{2s}(r_2) \tilde{\chi}_0(r_1, r_2) r_2^2 dr_2 \cdot \delta_{10} \cdot Y_{50}(\hat{k}_f) \equiv 0 \quad 6.44$$

Direct cross sections follow using eq.32 with eq.33 redefined as

$$P_2^{\sim}(1s-2s) = P_2(1s-2s) - 4 \int_0^\infty dr_1 \cdot j_2(k_f r_1) u_1(r_1) \int_0^\infty dr_2 R_{2s}(r_2) \left\{ r_2 \frac{\tilde{\chi}_2(r_1, r_2) \delta_1(r_1, r_2)}{(2l+1)} - \tilde{\chi}_0(r_1, r_2) \right\} \quad 6.45$$

### 1s-2p Scattering

1s-2p cross sections follow using eq.34 with eq.36 replaced by

$$\tilde{H}(s, \lambda) = H(s, \lambda) + 4 \int d\mathbf{r}_1, \mathbf{r}_2 \int_s(k; \mathbf{r}_1) \mu_\lambda(\mathbf{r}_1) \int d\mathbf{r}_2, \mathbf{r}_3 R_{2p}(\mathbf{r}_2) \cdot \\ \cdot \left\{ 3 \sum \left[ \frac{l \delta_{l-1}(\mathbf{r}_1, \mathbf{r}_2)}{(2l-1)} + \frac{(l+1) \delta_{l+1}(\mathbf{r}_1, \mathbf{r}_2)}{(2l+3)} \right] \tilde{\chi}_l(\mathbf{r}_1, \mathbf{r}_2) - \tilde{\chi}_l(\mathbf{r}_1, \mathbf{r}_2) \right\}$$

A check on the computational techniques is provided by replacing  $\mu_s(\mathbf{r})$  by  $\int_s(k; \mathbf{r})$  in eq. 45 and 46 and ignoring all exchange terms. The approximation then reduces to the Polarized Born approximation.

The fully symmetrised second order polarization approximation follows defining the higher order scattering amplitude to be

$$\tilde{T}_{it}^{(n)} \pm = \tilde{T}_{it}^{(n), d} \pm \tilde{T}_{it}^{(n), ex} \quad 6.47$$

such that

$$\tilde{T}_{it}^{(n), ex} = \frac{1}{2\pi} \langle \mathcal{E}_i(2) \exp(i \mathbf{k}_i \cdot \mathbf{r}_i) | \mathcal{Y}_{i_0} - \mathcal{Y}_{i_1} | Z^{(n)}(2, 1) \rangle = \frac{1}{2\pi} \{ I_5^* + I_6^* \} \quad 6.48$$

where

$$Z^{(n)}(2, 1) = \mathcal{D}^{(n)}(2, 1) F(2)$$

Cross sections are given replacing eq. 45 by

$$\tilde{P}_s(1s-2s) = \tilde{P}_s(1s-2s) \pm 4 \int d\mathbf{r}_1, \mathbf{r}_2 \int_s(k; \mathbf{r}_1) \int d\mathbf{r}_2, \mathbf{r}_3 \mu_s(\mathbf{r}_2) R_{2s}(\mathbf{r}_2) \cdot \\ \cdot \left\{ \frac{\tilde{\chi}_s(\mathbf{r}_2, \mathbf{r}_1)}{(2s+1)} - \sum_{l, l'} \frac{\langle ll'00 | s0 \rangle^2}{(2s+1)} \delta_{l'}(\mathbf{r}_1, \mathbf{r}_2) \tilde{\chi}_l(\mathbf{r}_2, \mathbf{r}_1) \right\} \quad 6.49$$

and eq. 46 by

$$\tilde{H}(s, \lambda) = \tilde{H}(s, \lambda) \pm 4 \int d\mathbf{r}_1, \mathbf{r}_2 \int_s(k; \mathbf{r}_1) \int d\mathbf{r}_2, \mathbf{r}_3 R_{2p}(\mathbf{r}_2) \mu_\lambda(\mathbf{r}_2) / (2s+1) \\ \cdot \left\{ \sqrt{3} \sum \langle ll'00 | s0 \rangle^2 \tilde{\chi}_l(\mathbf{r}_2, \mathbf{r}_1) \mathcal{Y}_l(\mathbf{r}_1, \mathbf{r}_2) - 3 \tilde{\chi}_s(\mathbf{r}_2, \mathbf{r}_1) \right\} \quad 6.50$$

The non-zero values of the squared Clebsch-Gordon coefficients

$\langle ll'00 | s0 \rangle^2$  are given below for  $l = 0, 1, 2$ .

	$l = 0$	$1$	$2$
$l' = s+2$			$3(l'+2)(l'+1)/(2l'+1)/(2l'+3)/2$
$s+1$		$l'/(2l'+1)$	
$s$	$1$		$4'(l'+1)/(2l'-1)/(2l'+3)$
$s-1$		$(l'+1)/(2l'+1)$	
$s-2$			$3l'(l'-1)/(2l'-1)/(2l'+1)/2$

In practice evaluation of the sums for the 1s-2s cross sections showed that it was necessary to retain these first three terms. Calculations with 1s-2p transitions converged very slowly as additional terms were introduced. No calculations were made using the full term of eq.50 for the 1s-2p case, but instead (46) was used.

Evaluation of eq.45, 46, 69 and 50 depended on the relationship

$$\iint \left\{ Y_{1t}(\hat{r}_1) P_{1t}(\hat{r}_1) P_{1t}(\hat{r}_2) \right\} Y_{\lambda_0}(\hat{r}) Y_{lm}(\hat{r}) d\hat{r}_1 d\hat{r}_2 \quad 6.51$$

$$= \sqrt{4\pi} / (2s+1) \cdot \langle l' l' 0 0 | s 0 \rangle^2 (s m | l m | \lambda 0) \delta_{\mu m}$$

where

$$(s m | l m | \lambda 0) = \left[ (2l+1) / (2s+1) \right]^{1/2} \langle s l 0 0 | \lambda 0 \rangle \langle s l m m | \lambda 0 \rangle$$

### 3. FULL POLARIZATION APPROXIMATION

The full polarization approximation total cross sections in the 1s-2s transition have been evaluated in both the full form, with direct and exchange distortion from the atomic wave function, and in the form neglecting the higher order exchange terms, which is consistent with the definition of F(1). (These results are given in table 6.3 as Full Polarization (dir)). Also available are the polarized Born Oppenheimer values which follow from the full polarization treatment upon replacing the single particle projectile function by a plane wave. If exchange terms are neglected in all orders the form would reduce to the polarized Born approximation described above. Full polarization (direct) cross sections are shown in fig. 6.20. At low energies below its peak, it is seen to exceed the cross sections of the close coupling approximation and experiment by a factor of two. The peak position is slightly above the other theoretical approximation peaks agreeing closely with the experimental peak position. At high energies ( $E = 9\text{ryd}$ ) (tab. 6.3) the cross sections approach the B.O. values from below.

The full polarization (direct and exchange) approximation is observed to considerably exceed the full polarization (direct) values at all but very low energies ( $E < 0.8$  ryd) (fig. 6.22). The reason for this can be seen by observing the behaviour of the symmetrised Born and polarized Born Oppenheimer approximations. The introduction of direct polarization into the B.O. approximation brings about a 20% reduction in these very large cross sections whereas exchange polarization produces a far greater movement of the B.O. curve in the opposite direction. Replacing the plane wave by the extended polarization single particle projectile wave function causes a considerable reduction in the cross sections particularly at low energies.

The complexity of the exchange polarization terms renders the full polarization (direct and exchange) approximation in the 1s-2p transition impractical. Furthermore the experience of the 1s-2s transition has indicated that this approximation produces excessively large values and it has not been attempted here. The full polarization (direct) cross sections are shown in fig. 6.23 alongside the polarized B.O. (direct) approximation and in fig. 6.21 in comparison with close coupling and experimental values. The latter suggests that the direct polarization has an excessive effect in reducing the symmetrised Born approximation at low energies. At higher energies these terms become less significant as the approximation tends to the B.O. approximation (tab. 6.4.)

A breakdown of total cross<sup>sections</sup> into partial contributions shows that the reduced magnitude in comparison with the single particle polarization cross section is a general feature (fig. 6.11 to 6.15). Due to the smaller role of the triplet contribution, the greater differences in cross sections of this symmetry in the total cross section, are not apparent particularly in the

s-wave. Shape and peak positions are common to all the approximations in significant partial cross sections.

## NUMERICAL TECHNIQUES

The integral expressions of the type (eq. 6.33 and 6.36)

$$I = \int_0^\infty dr_1 r_1^2 u(r_1) v(r_1) \int_0^\infty dr_2 r_2^2 \omega(r_2) \delta_s(r_1, r_2) \tilde{\chi}_s(r_1, r_2)$$

are evaluated numerically. Rewriting the integral as a sum of terms corresponding to the regions where  $r_2$  is less than and greater than  $r_1$  and using the conversion

$$\int_0^\infty dr_1 f(r_1) \int_{r_1}^\infty dr_2 g(r_2) = \int_0^\infty dr_2 g(r_2) \int_0^{r_2} dr_1 f(r_1),$$

provided that  $g$  and  $f$  are zero at the limits and integration, we have

$$I = \int_0^\infty dr_1 r_1^2 / r_1^{s+1} \left\{ u(r_1) v(r_1) \int_0^{r_1} dr_2 r_2^2 r_2^s \tilde{\chi}_s(r_2, r_1) \omega(r_2) \right. \\ \left. + \omega(r_1) \int_0^{r_1} dr_2 u(r_2) v(r_2) r_2^s \tilde{\chi}_s(r_1, r_2) r_2^2 dr_2 \right\}$$

Numerical integration is effected by Simpson's method

$$\int_{r_i}^{r_{i+2}} f(r) dr = h/3 [f(r_i) + 4f(r_{i+1}) + f(r_{i+2})]$$

The same intervals are used as for the solution of the integro-differential equation of  $\mu_s(r)$ .

In 1s-2s transitions all integrals are modified by an exponentially decaying term. This necessitates integration out to an upper limit  $R = 10$  a.u. for satisfactory convergence (6th figure). In 1s-2p transitions one direct term decays as the inverse fourth power of  $r$  for large  $r$ . (All other terms decay exponentially). The integrand, has not decayed sufficiently in the region beyond which sensible values are given for the numerical solution of the integro-differential equation. Instead the asymptotic single

particle wave function suggested by Burgess (eq. 4.103 and 4.104) is substituted and the asymptotic part of the integration continued to a point at which some convergence condition is satisfied (An error message is printed in the program if the error exceeds this condition).



CHAPTER 7.

CONCLUSION.

i) THE PRESENT WORK

It has been demonstrated (in Chapter 6.2) that good agreement is found between the extended polarization approximation calculations of cross sections, for both  $1s-2s$  and  $1s-2p$  transitions, and both the six-state close coupling approximation and experiment. The improved agreement over the adiabatic approximation appears to be due to the much smaller second order potential in the E.P. approximation. Those approximations which include only polarization and no distortion give excitation cross sections which are much too small, as has been demonstrated for the monopole suppression approximation (fig.5.4, 5.5.). Clearly monopole suppression is not a satisfactory alternative to the inclusion of distortion terms in the simple polarized orbital description of the  $e^- - H$  excitation processes.

At intermediate energies the  $1s-2s$  cross sections of the E.P. approximation and the experimental results of Hils et al (1966) do not compare so well, agreeing only in their indication of a second peak. More investigation of this peak might be rewarding. Though a more satisfactory approximation would be provided including higher order exchange terms in the projectile wave function it seems doubtful that this correction would significantly effect the disagreement. However, changes of the order of magnitude required to bring the E.P. approximation and experiment into line might be provided by introducing polarization into the transition matrix through the perturbed atomic wave function in the manner attempted in the full polarization approximation (c.f. ch. 6.3.) The investigation of the polarized Born approximation (c.f. ch. 6.1) has shown that large variations in the

magnitude of the cross sections results from neglect of various polarization terms in turn without significantly altering the shape of the cross section plot as a function of energy.

Unfortunately it is not possible to consistently include all polarization and distortion (direct and exchange) effects up to second order. Attempts to do so in the full polarization approximation produces cross sections that exceed the Born values, though this is shown by the polarized Born Oppenheimer approximation (whose results are even larger) to be the effect of the inadequate treatment of exchange rather than the effect of polarization. Since it has not proved possible to include all second order exchange effects in the projectile wave function a consistent zero order exchange approach is attempted in the full polarization (direct) approximation. Not only does this provide a reduction in the magnitude of the cross sections but it is also much less expensive in computer time. However, the result does not produce the required improvements to the E.P. approximation, though judicious neglect of some of the additional higher order terms might provide better values.

## 2) THE EXTENSION OF THE THEORY

Recently attempts have been made to correct for neglected terms of the truncated set of close coupled equations, based on hydrogen bound states, by inclusion of additional terms. The Burke, and Taylor (1967) method added a series of correlation terms depending on the electron-electron coordinate, which is not explicitly included in the close coupling approximation based on hydrogen bound states. The drawback of this approach is its failure to make full allowance for polarization, though results prove to be very good for ground state excitation to the  $n = 2$  level in the energy range up to the  $n = 3$  threshold resonance region.

It appears that an antisymmetrised expansion in polarized target eigenfunctions, following the lines of the close coupling approximation and polarized orbital methods would be promising. Consider the expansion

$$\Psi_i^+ = \sum_n (1 \pm P_{12}) \psi_n(1,2) F_n(1)$$

where

$$\psi_n(1,2) = \phi_n^{(0)}(2) \quad \text{for } n \neq 0$$

and

$$\psi_0(1,2) = \phi_0^{(0)}(2) + \phi_0^{(1)}(1,2)$$

$\phi_n^{(0)}$  are the hydrogen atom bound state wave functions and  $\phi_0^{(1)}$  is the first order perturbed orbital of the perturbed hydrogen ground state system. By truncating the sum to the first term ( $n = 0$ ) only, substitution into a variational form provides the extended polarisation approximation whilst replacing  $\psi_0(1,2)$  by  $\phi_0(2)$  provides the close coupling approximation. The Hahn (1964) condition for a bound on phases requires that  $\phi_0^{(1)}(1,2)$  is orthogonal to the included bound state functions.

In the adiabatic approximation it was apparent that full inclusion of the monopole term produced an excessive short range attraction. This might be remedied by considering an approximation which makes explicit allowance for the s-channels whilst including higher angular momentum channels within a polarized orbital framework.

### 3) AN EXTENSION TO MORE COMPLEX SYSTEMS

In the extension of the extended polarization approach for excitation cross sections to more complex systems than electron hydrogen scattering the following points are noteworthy:

The success of the E.P. approximation was shown by Callaway et al

(1968) in its application to electron helium (ground state) elastic scattering. Though the polarization potential is smaller ( $1.4 \text{ a}^3$ ) than  $e^- - \text{H}$  scattering ( $4.5 \text{ a}^3$ ), the external electron now sees a closed shell and polarization is expected to be more important than correlation.

In contrast with the electron helium (ground state) case, elastic scattering of an electron off Helium in the metastable  $2^3 \text{ S}$  state, with a much larger polarization potential ( $316 \text{ a}^3$ ), produces inferior results for cross sections in the E.P. approximation to those of the adiabatic dipole approximation (Sklarzew and Callaway - 1968). This may be seen as follows. The major omission of the E.P. approximation compared with the full polarized orbital method are in the perturbed exchange terms. For ground state scattering these are small and have little effect on cross sections. In the metastable state the perturbed wave function is large as the projectile electron nears the atom and such effects become significant leading to an excessively repulsive potential.

In the photoionisation of Helium the use of polarized orbital wave functions in the dipole length formulation provides more accurate oscillatory (wave functions, whilst the opposite is the case for electron scattering) strengths than the Hartree Fock continuum, on singly ionised Lithium. (Bell and Kingston, 1967). This may be explained as due to the short range failure of the polarized orbital approximation being sufficiently compensated for by its successful representation of long range polarization for photoionisation of Helium but not for  $\text{Li}^+$ .

APPENDIX 1. THE FULL (SLOAN) POLARIZED ORBITAL SCATTERING EQUATION

The radial equation for elastic scattering of  $e^-$  by  $H(1s)$  in full second order polarization treatment (direct and exchange), when determined in a manner consistent with the Temkin-Sloan approach, provides the scattering equation

$$\begin{aligned} & \left\{ \frac{d^2}{dr^2} + k_0^2 - \ell(\ell+1)/r^2 - 2\tilde{V}(r) - 2V_{pol}(r) + V_d(r) \right\} u_\ell(r) = \\ & \pm \left\{ (E_0 - k_0^2) \delta_{\ell 0} \int R(r_2) u_\ell(r_2) r_2 dr_2 + 2/(2\ell+1) \int R(r_2) u_\ell(r_2) \chi_\ell(r, r_2) r_2 dr_2 \right\} r_\ell R(r_\ell) \\ & \pm \left[ 4(E_0 - k_0^2) \left\{ R(r) \int \chi_\ell(r, r_2) u_\ell(r_2) r_2 dr_2 + \int R(r_2) \tilde{\chi}_\ell(r_2, r) u_\ell(r_2) r_2 dr_2 \right\} r_\ell / (2\ell+1) \right. \\ & \quad + 16(E_0 - k_0^2) r_\ell \left\{ \int \tilde{\chi}_\ell(r_1, r_2) \tilde{\chi}_\ell(r_2, r_1) u_\ell(r_2) r_2 dr_2 \right\} / (2\ell+1) \\ & \quad + 2r_\ell R(r_\ell) \delta_{\ell 0} \left\{ \tilde{V}(r) \int R(r_2) u_\ell(r_2) r_2 dr_2 + \int R(r_2) \tilde{V}(r_2) u_\ell(r_2) r_2 dr_2 \right\} \\ & \quad - 4r_\ell R(r_\ell) \left\{ \int R(r_2) \delta_\ell(r, r_2) u_\ell(r_2) r_2 dr_2 \right\} / (2\ell+1) \\ & \quad \left. + 2r_\ell \left\{ R(r) \int \tilde{V}(r_2) \tilde{\chi}_\ell(r, r_2) u_\ell(r_2) r_2 dr_2 + \tilde{V}(r) \int R(r_2) \tilde{\chi}_\ell(r_2, r) u_\ell(r_2) r_2 dr_2 \right\} / (2\ell+1) \right] \end{aligned}$$

All terms are defined in chapter 4, section one. Neglecting the term in square brackets on the right hand side gives the extended polarization equation (eq.4.20).

## APPENDIX 2. THE EVALUATION OF THE FIRST ORDER PERTURBED ORBITAL

We wish to find the most general solution to equation (6)(Ch.9) subject to the physical restriction of a finite solution, asymptotically and at the origin.

$$\text{For } s \neq 0 \\ \left( \frac{1}{r_2} \frac{d^2}{dr_1^2} r_2 - s(s+1)/r_1 + 2/r_2 - 1 \right) \tilde{\chi}_s(r_1, r_2) = r_2^s / r_1^{s+1} \cdot e^{-r_2} \quad A.1$$

A solution to the homogeneous equation can be found in the form of a series expansion

$$h = \exp(\pm r_2) \sum_{\mu} c_{\mu} r_2^{\mu+s}$$

Substituting this into the equ. A.1 and equating the coefficients of the different powers to exponentially decaying and increasing forms.

$$h_1 = e^{-r_2} \sum_{\nu=0}^{s+1} a_{\nu} r_2^{(\nu-s-1)} \quad \text{where} \quad a_{\nu} = \frac{-2 \cdot a_{\nu-1} (2-\nu-s)}{\nu(\nu-2s-1)} \quad A.2$$

and

$$h_2 = e^{r_2} \sum_{\nu=0}^{s-1} b_{\nu} r_2^{(\nu-s+1)} \quad \text{where} \quad b_{\nu} = \frac{-2 \cdot b_{\nu-1} (\nu-s)}{\nu(\nu-2s-1)}$$

In particular  $a_{s+2} = 0$  and  $b_s = 0$ .  $a_0$  and  $b_0$  are arbitrary and chosen as unity. For the inhomogeneous equation there are two solutions depending whether  $r_1$  is greater or less than  $r_2$ . The equation may be solved by assuming the form

$$y = \exp(-r_2) \cdot g(r_1) \cdot r_2^s / r_1^{s+1} \quad A.3$$

It can be shown by substitution into the equ. A.1 that  $g$  is a linear function

$$g_< = -\frac{1}{2} \left[ \frac{1}{s} + r_2 / (s+1) \right] \quad \text{if } r_1 > r_2 \quad A.4$$

$$g_> = -\frac{1}{2} \left[ \frac{1}{(s+1)} + r_2 / s \right] \quad \text{if } r_1 < r_2$$

Combinations of the homogenous and inhomogenous solutions are taken to provide a function which is well behaved at the boundaries. Consequently we choose the general form

$$\tilde{\chi}_s(r_1 > r_2) = \alpha(r_1) \{h_1 - h_2\} + e^{-r_1} r_1^s \cdot g_s / r_1^{s+1} \quad A.5$$

and

$$\tilde{\chi}_s(r_1 < r_2) = \beta(r_1) \cdot h_1 + e^{-r_1} r_1^s g_s / r_1^{s+1}$$

Of the homogenous solutions only  $h_1$  can guarantee a finite asymptotic solution in the region  $r_2 > r_1$ . The combination  $(h_1 - h_2)$  has a leading term of order  $r_1^s$  for small  $r_1$ , and provides a finite solution at the origin in the region  $r_1 > r_2$ . Asymptotically  $h_2$  increases exponentially. It is essential that  $\alpha(r_1)$  should be chosen to decay fast enough to counter this behaviour.  $\beta(r_1)$  should be chosen to cancel the singularity of  $h_1$  at the origin. Satisfactory solutions can be found while requiring that the two solutions for  $r_2$  greater and less than  $r_1$  should be continuous both in themselves and with respect to their derivatives at their boundary point  $r_1 = r_2$ .

$$\alpha(r_1) = \frac{-\sum_{\nu=0}^{s+1} a_\nu (\nu-s-1) r_1^{(\nu-s-2)} (1+r_1) e^{-2r_1} / (2r_1) \cdot (2s+1)/s/(s+1)}{\sum_{\nu=0}^{s+1} \sum_{\mu=0}^{s-1} (\nu-\mu-2r_1) a_\nu b_\mu r_1^{(2\nu-2s-3+\mu)}} \quad A.6$$

and

$$\beta(r_1) = \alpha(r_1) + \frac{\sum_{\nu=0}^{s-1} b_\nu (\nu-s-1+2r_1) (1+r_1) / (2r_1) \cdot (2s+1)/s/(s+1)}{\sum_{\nu=0}^{s+1} \sum_{\mu=0}^{s-1} a_\nu b_\mu (\nu-\mu-2r_1) r_1^{(\mu+\nu-2s-1)}}$$

The coefficients  $a_\nu$  and  $b_\nu$  have been defined previously.

Note that  $\alpha(r_1)$  decays asymptotically as  $\exp(-2r_1)$ . The leading term of

$\beta(r_1)$  goes as  $r_1^s$  for small  $r_1$ .

For  $s = 0$  the homogeneous solution to  $h$  satisfies

$$\left[ \frac{d^2}{dr_1^2} + \frac{2}{r_1} - 1 \right] r_1 \cdot h(r_1) = 0$$

An equivalent pair of first order differential equations can be written

$$z = (D - \frac{1}{r_1} - 1)g \quad \text{and} \quad (D + \frac{1}{r_1} - 1)z = 0 \quad A.7$$

where D is the single derivative operator and  $g \equiv r_1 \cdot h$ . The solution to the second of these equations is

$$z = C \cdot \exp(r_1) / r_1 \quad A.8$$

If  $C \neq 0$

$$D(z \cdot g) = z \cdot Dg + g(1 - \frac{1}{r_1}) \cdot z = z \cdot z \quad A.9$$

Substituting for Z and operating with  $D^{-1}$  gives

$$h = C \left\{ -e^{r_1} / r_1 + 2e^{-r_1} Ei(2r_1) \right\} \quad A.10$$

where

$$Ei(2r) = \int_{-\infty}^r e^{2\rho} / \rho \cdot d\rho$$

For small values of r

$$Ei(2r) \rightarrow ce + \ln(2r) + 2r + r^2 + \dots$$

ce is Eulers constant. A detailed account of this function can be found in Abramowitch and Stegun (1965).

If  $C = 0$  then  $g = x$

where

$$Dx = (\frac{1}{r_1} - 1) \cdot x$$

which gives  $h = e^{-r_1}$

A.11

For the inhomogeneous equation  $(D^2 + 2/r_1 - 1)w = f(r_1)$ , the equivalent first order pair is

$$(D - \frac{1}{r_1} + 1)w = p \quad \text{and} \quad (D + \frac{1}{r_1} - 1)p = f(r_1) \quad A.12$$



From (A.11)

$$D(x, p) = x \cdot f(r_2) \quad A.13$$

Likewise A.9 gives

$$D(z, \omega) = z \cdot p \quad A.14$$

Operating on both equations with  $D^{-1}$  and substituting for  $p$  gives

$$\omega = z^{-1} \int_0^{r_2} e^{z\rho/\rho^2} d\rho \int_0^\rho e^{-\rho'} \rho' f(\rho') d\rho' \quad A.15$$

For the region  $r_1 > r_2$ ,  $f(r_2) = e^{-r_2} r_2 [-r(r_2) + 1/2]$ . In (15) this gives

$$y_< = -1/4 [1/2 - r(r_2)] e^{-r_2} \{2r_2 + 2 \ln(r_2) - 1 - 1/2\} \quad A.16$$

There is some freedom in the choice of the constants of integration as these relate to the homogeneous solutions of the equation. Though  $y_< \rightarrow 1/r_2$  as  $r_2 \rightarrow 0$ , a combination of  $y_<$  with the homogeneous solution  $(1/2 - r(r_2)) \cdot h_1/4$  tends to a non-zero finite limit.

The most general solution is

$$\tilde{x}(r_1 > r_2) = y_< + 1/4 (1/2 - r(r_2)) h_1 + \alpha(r_2) h_2 \quad A.17$$

If  $r_1 < r_2$ ,  $f(r_2) = -[r_2 r(r_2) - 1] e^{-r_2}$ . A solution of (15) is provided by

$$y_> = 1/4 [(1/2 - 2 \ln(r_2) - 1) - r(r_2) (1/2 + 1 - 2 \ln(r_2) - 2r_2)] e^{-r_2} \quad A.18$$

This solution is well behaved at the boundaries. The most general solution takes the form

$$\tilde{x}(r_1 < r_2) = y_> + \beta(r_2) \cdot h_1 \quad A.19$$

Imposing the continuity condition to the solutions and their derivatives at the boundary  $r_1 = r_2$ , demands that

$$\alpha(r_2) = -(1 + 1/2r_2) e^{-2r_2} (ce + \ln(2) + 1/2 \ln(r_2)) + 1/4 e^{-2r_2} (1/2 + 2 - 2r_2) + 1/2 (1 - 1/2r_2) E_1(2r_2) \quad A.20$$

and

$$\beta(r_2) = \alpha(r_2) + 1/4 [2e^{-r_2} (1 + 1/2r_2) E_1(2r_2) + 2 (1 - 1/2r_2) \ln(r_2) - (1 + 1/2r_2)]$$

where  $E_1(2r) = \int_0^\infty e^{-2\rho/\rho} d\rho$ . (See previous reference to Abramowitch and Stegun.).

For small  $r$

$$E_1(2r) \rightarrow -ce - \ln(2r) + 2r + r^2 + \dots$$

As the solutions used in this work include  $s = 1$  and  $s = 2$ , the terms  $\alpha$ ,  $\beta$ ,  $h_1$  and  $h_2$  will be given in simpler form. With reference to equations (5), (2) and (6).

For  $s = 1$

$$\alpha_1 = -3/8 \cdot e^{-2r} (1 + 1/r)^2 \quad A.21$$

$$\beta_1 = \alpha_1 - 3/8 (1 - 1/r^2)$$

$$h_1 = e^{-r} (1 + 2r + 2r^2) / r^2$$

$$h_2 = e^r / r^2$$

For  $s = 2$

$$\alpha_2 = 5/4 e^{-2r} (1 + r) (3 + 3r + r^2) / r^3 \quad A.22$$

$$\beta_2 = \alpha_2 + 5/4 (1 + r) (3 - 3r + r^2) / r^3$$

$$h_1 = e^{-r} (1 + 3r/2 + r^2 + r^3/3) / r^3$$

$$h_2 = e^r (1 - r/2) / r^3$$

In the course of the problems met with in this work it is necessary to impose the condition that the final state of the atomic system be orthogonal to the initial state. For scattering to a final state where <sup>the</sup> wave function is given by  $\psi_f = R_{nl}(r) Y_{lm}(r)$  this condition can be satisfied by redefining  $\psi^{(n)}$  by

$$\psi^{(n)}(1, 2)' = \psi^{(n)}(1, 2) - c(1) \psi_f(2)$$

where

$$c(1) = \int \psi_f^*(2) \psi^{(n)}(1, 2) d\underline{r}_2$$

For scattering to the 2s-state the non-s-wave terms of  $\psi^{(n)}$  are already

orthogonal. The s-wave term becomes

$$\tilde{\chi}_0(r_1, r_2)' = \tilde{\chi}_0(r_1, r_2) - C_{2s}(r_1) R_{2s}(r_2) \quad A.23$$

where

$$C_{2s}(r_1) = -2^{5/2} (2 + 3r_1) e^{-3r_1/2} / 81$$

Likewise for 2p scattering the p-wave term is redefined as

$$\tilde{\chi}_1(r_1, r_2)' = \tilde{\chi}_1(r_1, r_2) - C_{2p}(r_1) R_{2p}(r_2) \quad A.24$$

where

$$C_{2p}(r_1) \cdot R_{2p}(r_2) = \frac{16r_1 e^{-r_1/2}}{729 \cdot r_1^2} \left[ 8 - e^{-3r_1/2} (8 + 12r_1 + 9r_1^2 + 27r_1^3/4) \right]$$

### APPENDIX 3. THE COMPUTER PROGRAM

The Program is divided into subroutines. Control is directed from the main routine.

#### 1) DIRECT

Reads parameters which determine the approximation:

KISQ = incident energy (ryd); L = orbital angular momentum (units of  $\hbar = 1$ );  
 KP = parity; k0, k1, k2 = (s = 0, 1, 2) partial polarization potentials;  
 k3, k4 = (s = 0, 1) partial distortion potentials; HX(1) = primary radial interval. KX1, KX2, KED, KOR relate to terms kept in excitation cross section (see below). The main routine calls subroutines as follows.

#### 2) RADIAL

Assigns values to the radial parameter RX(k) for k = 1 to 440 such that

$$RX(k) = RX(k-1) + HX$$

where HX = HX(1) initially, and HX doubles at the points k = 40, 140, 240

Calls subroutine EXFUN - Exfun evaluates the exponential functions EI (eq. A.10) and Ei (eq. A.20) at points corresponding to k = 1 to 440

These are required by the partial polarization and distortion potential called by subroutines VPOL0, VPOL1, VPOL2 (polarization) and D0, D1 (distortion) according to the values k0, k1, k2, k3, k4.

The total potential is assigned to POTENT(k) at successive points k = 1 to 440 in terms of the polarization and distortion potentials and the coulomb potential.

$$POTENT = -2\tilde{V}(1) + 2.Vpol(1) + Vd(1)$$

3) STASOL - evaluates the first three points (i = 1, 2, 3) of the two solution ( $\epsilon = 1$  and  $\epsilon = 0$ ) of  $u_i(k)$  of eq. 4.66 using the series expansion eq. 4.71.

4) FOXG01/FOXG02 - evaluates  $u_i(k)$  from k = 3 to 440 using the Fox Goodwin

technique (eq.4.69). The series values of  $u_1$  at  $k = 1$  and  $k = 2$  (from Stasol) determine  $u_1$  at  $k = 3$ . This is required to agree with the series  $u_1(3)$  (from Stasol) to the fifth figure for the program to continue. The integral functions  $g(k)$  (eq.4.69) depend on  $u_1(J)$  ( $J < k$ ) and are evaluated in GEES.

#### 6) GEES

The values of  $g(k)$  for  $k \leq 6$  are given by a series expansion (eq. 4.74 and 4.75). Values of  $g(k)$  for  $k \geq 6$  are given by the Newton Cotes formula (eq. 4.70). The two forms are compared at  $k = 6$ . The program continues if agreement is found to the fifth figure.

7) RHOS - the two solutions  $u_1(k)$  are combined linearly (eq.4.65a) to give a solution to the scattering equation (4.61).

8) PHASE - the solution is normalised to the asymptotic form

$$u_1 \sim k^{-1/2} \sin(kr - l\pi/2 + \delta_l)$$

Using eq.4.86. The phase shift is determined by comparing this form with the analytic asymptotic form derived by Burgess (eq.4.83)

9) XSEC - ( $kX1 = 1$ ) evaluates partial 1s-2s cross sections numerically (eq.6.32), using the previously determined normalised values of  $u_1(k)$ , with the Simpson integration technique. The bessel integral  $J_{N_f}^{(1)}(k)$  (eq.2.29) is evaluated numerically with the Simpson technique and checked by comparing the essentially asymptotic  $J_{N_f}^{(1)}(440)$  with the analytically derived value, (as the upper limit of integration tends to infinity). The additional polarization terms required by the full polarization approximation (eq.6.49) are evaluated numerically in DEXDAM.

10) XPEC - ( $kX2 = 1$ ) evaluates partial 1s-2p cross sections (eq.6.36) by the Simpson integration technique. The non-exponentially decaying asymptotic term (eq.4.109) is evaluated in the subroutine EXTRA. Additional polarizati

terms required by the full polarisation approximation (eq.6.50) are evaluated numerically in DEPDAM.

KED controls the included polarization terms in XSEC and XPEC (KED = 1 - direct). (KED = 3 - direct + exchange) (see section 3, chapter 6).

KOR = 1 requires that the initial and final wave functions are orthogonal

$\int \phi_f(2) \cdot \phi^{(1)}(1,2) d\underline{r}_2 = 0$  . Otherwise the first, <sup>order</sup> perturbed orbital is as

defined by eq.4.32.

-Consider the T-matrix element for the scattering of a hydrogen atom from the ground state to the 2p state with azimuthal and magnetic quantum numbers  $(l, m)$

$$T = \langle \psi_f | V | \Psi_i^+ \rangle \quad A4.1$$

keeping only those direct and exchange terms arising from the effect of zero and first order perturbed orbitals of  $\Psi_i^+$  the T-matrix is

$$T = \frac{1}{2\pi} \{ I_0 + I_1 + I_2 + I_3 + I_4 + I_5 + I_6 \} \quad A4.2$$

Using the expansions of  $\psi^{(1)}$ ,  $V$  and  $F$  (eq. 2.14, 2.17, 2.18) it follows that

$$\begin{aligned} I_0 &= \langle \psi_{2p,m}(2) e^{ik_f r_2} | \frac{1}{r_1} | \psi_{1s}(1) F^\pm(2) \rangle \quad A4.3 \\ &= \iint \sum_{s,\mu} (-i)^s j_s(k_f r_1) 4\pi Y_{s\mu}^*(\hat{k}_f) Y_{s\mu}(\hat{r}_1) R_{1s}(r_1) Y_{00}(\hat{r}_1) \\ &\quad \times R_{2p}(r_2) Y_{lm}^*(\hat{r}_2) \int_{\lambda} \mu_{\lambda}(r_2) Y_{\lambda 0}(\hat{r}_2) r_2 dr_2 \\ &= 4\pi \int \sum_{s,\mu} (-i)^s \int dr_1 r_1 j_s(k_f r_1) R_{1s}(r_1) \int R_{2p}(r_2) \mu_{\lambda}(r_2) r_2 dr_2 (sm|1m|\lambda 0) \delta_{s0} Y_{sm}^*(\hat{k}_f) \end{aligned}$$

(zero order exchange, electron-nucleon)

$$I_1 = \langle \psi_{2p,m}(2) e^{ik_f r_2} | \frac{1}{r_2} | \psi_{1s}(2) F^\pm(1) \rangle \quad A4.4$$

$$\begin{aligned} &= \iint \sum_{s,\mu} (-i)^s j_s(k_f r_1) 4\pi Y_{s\mu}(\hat{r}_1) Y_{s\mu}^*(\hat{k}_f) \int_{\lambda} \mu_{\lambda}(r_1) Y_{\lambda 0}(\hat{r}_1) r_1 \\ &\quad \times r_2^2 R_{2p}(r_2) Y_{lm}^*(\hat{r}_2) R_{1s}(r_2) Y_{00}(\hat{r}_2) \int_{\ell m} \delta_{\ell}(1,2) C_{\ell m}^*(\hat{r}_1) C_{\ell m}(\hat{r}_2) dr_1 dr_2 d\Omega_1 d\Omega_2 \\ &= 4\pi \int \sum_{s,\mu} (-i)^s \int dr_1 r_1 j_s(k_f r_1) \mu_{\lambda}(r_1) \int dr_2 r_2^2 R_{2p}(r_2) \delta_{\ell}(1,2) R_{1s}(r_2) \frac{\sqrt{3}}{2} (sm|1m|\lambda 0) Y_{sm}^*(\hat{k}_f) \end{aligned}$$

(zero order direct, electron-electron)

$$I_2 = \langle \psi_{2p,m}(2) e^{ik_f r_2} | \frac{1}{r_1} | \psi_{1s}(1) F^\pm(2) \rangle \quad A4.5$$

$$\begin{aligned} &= \iint \sum_{s,\mu} (-i)^s 4\pi j_s(k_f r_1) Y_{s\mu}(\hat{r}_1) Y_{s\mu}^*(\hat{k}_f) R_{1s}(r_1) Y_{00}(\hat{r}_1) r_1^2 \\ &\quad \times r_2 R_{2p}(r_2) Y_{lm}^*(\hat{r}_2) \int_{\lambda} \mu_{\lambda}(r_2) Y_{\lambda 0}(\hat{r}_2) \int_{\ell m'} C_{\ell m}^*(\hat{r}_1) C_{\ell m'}(\hat{r}_2) \delta_{\ell}(1,2) dr_1 dr_2 d\Omega_1 d\Omega_2 \\ &= 4\pi \int \sum_{s,\mu} (-i)^s \int dr_1 r_1^2 j_s(k_f r_1) R_{1s}(r_1) \int dr_2 r_2 R_{2p}(r_2) \mu_{\lambda}(r_2) \delta_{\ell}(1,2) \frac{\sqrt{3}}{(2s+1)} (sm|1m|\lambda 0) Y_{sm}^*(\hat{k}_f) \end{aligned}$$

(zero order exchange, electron-electron)

$$\begin{aligned}
 I_3 &= \langle \mathcal{O}_{2p,m}(2) e^{ik_f \cdot r} | Y_{1,2} | \mathcal{D}^{(1)}(1,2) F(1) \rangle \quad A4.6 \\
 &= \iint \int_{S_A} (-i)^5 4\pi f_s(k_f r_1) Y_{2,0}^*(\hat{r}_1) Y_{2,0}(\hat{r}_1) \int \mu_{1,2}(r_1) Y_{2,0}(\hat{r}_1) r_1 \\
 &\quad * r_2^2 R_{2p}(r_2) Y_{1m}(\hat{r}_2) \int \tilde{\chi}_{l'}(1,2) P_{l'}(\hat{r}_{12}) \int \delta_l(1,2) R_l(\hat{r}_{12}) dr_1 dr_2 d\Omega_1 d\Omega_2 \\
 &= 4\pi \int_{S_A} (-i)^5 \int dr_1 r_1 f_s(k_f r_1) \mu_{1,2}(r_1) \int dr_2 r_2^2 R_{2p}(r_2) \delta_l(1,2) \tilde{\chi}_{l'}(1,2) \frac{4\sqrt{3}}{(2l'+1)} \\
 &\quad (first order direct, electron-electron) * \langle l100 | l'0 \rangle^2 (s_m | 1m | \lambda_0) Y_{sm}^*(\hat{r}_f)
 \end{aligned}$$

where

$$\langle l100 | l'0 \rangle = 1/(2l+1) [l' S(l'-1, l) + (l+1) S(l'+1, l)] \quad A4.7$$

$$\begin{aligned}
 I_4 &= \langle \mathcal{O}_{2p,m} e^{ik_f \cdot r} | Y_{1,1} | \mathcal{D}^{(1)}(1,2) F(1) \rangle \quad A4.8 \\
 &= \iint \int_{S_A} (-i)^4 4\pi f_s(k_f r_1) Y_{2,1}^*(\hat{r}_1) Y_{2,1}(\hat{r}_1) \int \mu_{1,2}(r_1) Y_{2,1}(\hat{r}_1) \\
 &\quad * r_2^2 R_{2p}(r_2) Y_{1m}(\hat{r}_2) \int \tilde{\chi}_{l'}(1,2) P_{l'}(\hat{r}_{12}) dr_1 dr_2 d\Omega_1 d\Omega_2 \\
 &= 4\pi \int_{S_A} (-i)^4 \int dr_1 f_s(k_f r_1) \mu_{1,2}(r_1) \int dr_2 r_2^2 R_{2p}(r_2) \tilde{\chi}_{l'}(1,2) \frac{4\sqrt{3}}{3} (s_m | 1m | \lambda_0) Y_{sm}^*(\hat{r}_f)
 \end{aligned}$$

(first order direct, electron nucleon)

$I_4 = 0$ , if the orthogonality condition  $\langle R_{2p} | \mathcal{D}^{(1)} \rangle = 0$  is applied  
(see eq. 6.42.)

$$\begin{aligned}
 I_5 &= \langle \mathcal{O}_{2p,m} e^{ik_f \cdot r} | Y_{1,2} | \mathcal{D}^{(1)}(2,1) F(2) \rangle \quad A4.9 \\
 &= \iint \int_{S_A} (-i)^5 4\pi f_s(k_f r_1) Y_{2,0}^*(\hat{r}_1) Y_{2,0}(\hat{r}_1) \int \tilde{\chi}_{l'}(2,1) P_{l'}(\hat{r}_{12}) r_1^2 \\
 &\quad * r_2 R_{2p}(r_2) Y_{1m}(\hat{r}_2) \int \mu_{1,2}(r_2) Y_{2,0}(\hat{r}_2) \int \delta_l(1,2) P_l(\hat{r}_{12}) dr_1 dr_2 d\Omega_1 d\Omega_2 \\
 &= 4\pi \int_{S_A} (-i)^5 \int dr_1 r_1^2 f_s(k_f r_1) \int dr_2 r_2 R_{2p}(r_2) \tilde{\chi}_{l'}(2,1) \delta_l(1,2) \frac{4\sqrt{3}}{(2s+1)} \mu_{1,2}(r_2) \\
 &\quad * (l l' 00 | s 0) (s_m | 1m | \lambda_0) Y_{sm}^*(\hat{r}_f)
 \end{aligned}$$

(first order exchange, electron-electron)

Values of  $(l l' 00 | s 0)$  have been given for  $l = 0, 1, 2$

in chapter 6.3



$$I_b = \langle \mathcal{O}_{ep,m} e^{ik_f t} | \chi_i | \mathcal{O}^{(n)}(z,1) F(2) \rangle \quad A4.10$$

$$= \iint_{s,\mu} (-i) 4\pi f_s(k_f r_1) Y_{s\mu}(r_1) Y_{s\mu}^*(k_f r_1) \int_{\lambda_1} \tilde{\chi}_i(z,1) P_{\lambda_1}(r_1) r_1 \\ \cdot r_2 R_{2p}(r_2) Y_{1m}(r_2) \int_{\lambda_2} \mu_{\lambda}(r_2) Y_{\lambda_2}(r_2) dr_1 dr_2 dR_2 d\Omega_2 \\ 4\pi \int_{s,\lambda} (-i)^s \int dr_1 r_1 f_s(k_f r_1) \int dr_2 r_2 R_{2p}(r_2) \tilde{\chi}_s(z,1) \mu_{\lambda}(r_2) \frac{4\sqrt{3}}{(2s+1)} (sm | 1m | \lambda_0) Y_{sm}^*(k_f r_1)$$

(first order exchange, electron nucleon.)

We can rewrite the T-matrix

$$T = \frac{2}{\sqrt{3}} \int_{s,\lambda} (-i)^s Y_{sm}^*(k_f) (sm | 1m | \lambda_0)^* H(s,\lambda) \quad A4.11$$

where

$$H(s,\lambda) = \iint dr_1 dr_2 r_1 r_2 \mu_{\lambda}(r_1) \\ \cdot \left\{ R_{1s}(r_2) \left[ R_{2p}(r_2) f_s(k_f r_1) r_2 \delta_{1,1}(1,2) \pm R_{2p}(r_1) f_s(k_f r_2) [3r_2 \delta_s(1,2) - 3\delta_{s0}] / (2s+1) \right. \right. \\ \left. \left. + 4R_{2p}(r_2) f_s(k_f r_1) \left[ 3 \sum_{\lambda_1} \left[ \frac{1\delta_{\lambda_1-1}(1,2)}{(2\ell-1)} + \frac{(\ell+1)\delta_{\lambda_1+1}(1,2)}{(2\ell+3)} \right] r_2 \tilde{\chi}_{\ell}(1,2) / (2\ell+1) - \tilde{\chi}_{\ell}(1,2) \right] \right. \right. \\ \left. \left. \pm 4R_{2p}(r_1) f_s(k_f r_2) / (2s+1) \left[ \tilde{\chi}_s(1,2) - \sum_{\ell'} r_2 \langle \ell' 0 \ell' 1 s_0 \rangle^2 \delta_{\ell'}(1,2) \tilde{\chi}_{\ell'}(1,2) \right] \right\} \quad A4.12$$

Then the total cross section, summed over all m states, and including appropriately weighted singlet and triplet contributions, is

$$Q(1s \rightarrow 2p) = \sum_m k_f / 4k_i \left\{ |T^+|^2 + 3 |T^-|^2 \right\} d\vec{k}_f \quad (a_0^2) \quad A4.13 \\ = k_f / 3k_i \left\{ P^+ + 3P^- \right\} \quad A4.14$$

where

$$P^{\pm} = \sum_{s,m} \left\{ \sum_{\lambda} (sm | 1m | \lambda_0) H_m(s,\lambda) \right\}^2 \quad A4.15$$

$$= \sum_s \frac{1}{(2s+1)} \left\{ 2 \left[ \bar{H}(s,s+1) - \bar{H}(s,s-1) \right]^2 \frac{s(s+1)}{2} + \left[ (s+1) \bar{H}(s,s+1) + s \bar{H}(s,s-1) \right]^2 \right\} \quad A4.16$$

where  $\bar{H}(s,\lambda) = H(s,\lambda) / (2\lambda+1)^{1/2}$  A4.17

$$\therefore P^{\pm} = \sum_s \{ (s+1) \bar{H}(s, s+1)^2 + s \bar{H}(s, s-1)^2 \}$$

$$= \sum_{\lambda} \{ \lambda \bar{H}(\lambda-1, \lambda)^2 + (\lambda+1) \bar{H}(\lambda+1, \lambda)^2 \}$$

A4.18

Renormalising the asymptotic form of  $u_{\lambda}$  to that of a spherical bessel function the total cross section is

$$Q(1s \rightarrow 2p) = 4k_f / 3k_i [P^+ + 3P^-] \quad (\pi a_0^2)$$

A4.19

where

$$P^{\pm} = \sum_{\lambda=0}^{\infty} \{ \lambda H(\lambda-1, \lambda)^2 + (\lambda+1) H(\lambda+1, \lambda)^2 \}$$

A4.20

and  $H(s, \lambda)$  is given in eq. A4.

1.1 P-wave phase shifts (radians) ( $e^- - H$ )

a) singlet      b) triplet

- i) ---- polarised orbital (unmodified - Temkin and Lamkin 1961)
- ii) — p.o-polarised orbital (modified - Sloan 1964)
- iii) — e.a.-exchange adiabatic (Temkin and Lamkin 1961)
- iv) — e-central field exchange (John 1960)
- v) . . . 1s-2s-2p close coupling (Burke and Schey 1962)
- vi) --- extended polarisation (Callaway et al 1968)

1.2 Singlet S-wave phase shifts ( $e^- - H$ )

Close coupling Approximation - From Burke, Ormonde, Whitaker (1967)

- i) ---- 6 - state      (1s-2s-2p-3s-3p-3d)
- ii) --- 3 - state      (1s-2s-2p)
- iii) — 3 - state + correlation

1.3 Momentum Transfer Cross Sections ( $e^- - He$ ) (Callaway et al 1968)

- i) AED - Exchange Adiabatic (dipole only)
- ii) AET - Exchange Adiabatic (total)
- iii) EP - Extended Polarisation
- iv) Crompton, Elford, Jory (experimental)

1.4 Total Cross Sections (elastic) ( $e^- - He$ ) (Callaway et al - 1968)

- i) AED - Exchange Adiabatic (dipole)
- ii) AET - Exchange Adiabatic (total)
- iii) EP - Extended polarisation
- iv) Golden and Bandel (experimental) (1965)

## 1.5 Total Elastic Cross Sections ( $e^- - H$ )

- i) EP - Extended Polarisation (Present calculation)
- ii) PO-Polarised orbital (Modified - Temkin and Lamkin (1961) - Sloan (1964))
- iii) AET - Exchange <sup>Adiabatic</sup><sub>A</sub>(total) (present calculation)
- iv) MS - Monopole Suppressed (Present calculation)

## 2.1 Total Cross Sections ( $e^- - H$ ) (1s-2s)

- i) Born
- ii) Born Oppenheimer ( $BO^+$  singlet,  $BO^-$  triplet,  $BO^+$  total)
- iii) Central Field Exchange ( $EA^+$  singlet,  $EA^-$  triplet)

## 2.2 Total Cross Sections ( $e^- - H$ ) (1s-2p)

- i) Born
- ii) Born Oppenheimer ( $BO^+$  singlet,  $BO^-$  triplet,  $BO^+$  total)

## 2.3. Total Cross Sections ( $e^- - H$ ) (1s-2s)

- A) Rudge - Ochkur Approximation (1965)
- B) Experimental values - Stebbings et al (1960)
- C) Experimental values - renormalised to Fite (1968) recommended peak.

## 2.4 Total Cross Sections ( $e^- - H$ ) (1s-2p)

From Crothers and McCarrol (1965)

Vainshtein Approximation

- A)  $\nu' = -1/K_f$  no exchange
- B)  $\nu' = -1/(K_f - i\sqrt{\epsilon})$  no exchange
- C)  $\nu' = -1/(K_f - i\sqrt{\epsilon})$  with exchange
- D) Born
- X Crothers (1967)
- O,  $\Delta$  Experiment - Fite et al (1958, 1959)

2.5. Total Cross Sections ( $e^- - H$ ) (1s-2s)

Close Coupling - from Burke and Taylor (1967)

- i) - - - - - 6- state (1s-2s-2p-3s-3p-3d)
- ii) - - - - - 3- state (1s-2s-2p)
- iii) - - - - - 3- state + correlation

2.6. Total Cross Sections ( $e^- - H$ ) (1s-2p)

Close Coupling - From Burke and Taylor (1967)

- i) - - - - - 6- state (1s-2s-2p-3s-3p-3d)
- ii) - - - - - 3- state (1s-2s-2p)
- iii) - - - - - 3- state + correlation

FIG. 3.1 Intercomparison of relative measurements for excitation of hydrogen atoms into the metastable 2s state, including cascade contributions.

□ Hils, Kleinpoppen, and Koschmeider (1966)

⊕ Lichten and Schultz (1959)

△ Stebbings, Fife, Hummer and Brackmann (1961)

EP.- Extended Polarization (present calculation)

FIG. 3.2 Total Cross Sections for 1s-2s excitation of hydrogen atoms by electron collision

Theoretical curve (Burke, Taylor, Ormonde, Whitaker - 1967)

Same Folded with a Gaussian beam distribution

I Estimated spread of experimental values (Lichten and Schultz)

FIG. 3.3. Perpendicular Cross Sections for 1s-2p excitation of hydrogen atoms by electron collision.

Theoretical curve (Burke, Taylor, Ormonde, Whitaker - 1967)

Same Folded with Gaussian Beam distribution

I Experimental values (Chamberlain et al - 1964)

FIG. 3.4 Relative measurements of the cross section for excitation of the  $2p \rightarrow 1s$  transition in atomic hydrogen

- O Fite and Brackmann (1958)
- + Long, Cox and Smith (1967)
- 1) Born Approximation
- 2) Born Approximation with cascading
- 3)  $1s-2s-2p$  close coupling (Burke, Schey and Smith, 1963)

FIG. 3.5. Polarisation of Perpendicular Lyman  $\alpha$  radiation induced by electron impact.

FIG. 4.1. Polarization and distortion potentials as a function of the radial distance.

- 1)  $V_{pol}^{(0)}$  = Monopole polarization potential.
- 2)  $V_{pol}^{(1)}$  = Dipole polarization potential.
- 3)  $V_{pol}^{(2)}$  = Quadrupole polarization potential.
- 4)  $V_d^{(0)}$  = Monopole distortion potential
- 5)  $V_d^{(1)}$  = Dipole distortion potential.
- 6)  $\sum$  - total polarization plus distortion potential.

FIG. 4.2 Polarization and distortion potentials as a function of radial distance.

- 1)  $V_d$  - total distortion potential.
- 2)  $V_{pol}$  - total polarization potential.
- 3)  $V_t$  - total polarization plus distortion potential.

FIG. 4.3. s-wave phase shifts ( $e^- - H$ )

a) singlet                      b) Triplet

- 1) E.P - extended polarization (Callaway et al - 1968)
- 2) AED - exchange adiabatic dipole (Callaway et al - 1968)
- 3)  $\beta = 0$  - Monopole suppressed adiabatic potential (presnet calculation)
- 4)  $\beta = 1$  - Full adiabatic potential (present calculation)

FIG. 4.4. p-wave phase shifts ( $e^- - H$ )

a) Singlet      b) Triplet

- 1) E.P. - extended polarization approximation (Callaway et al - 1968)
- 2) AED - exchange adiabatic dipole (Callaway et al - 1968)
- 3)  $\beta^3 = 0$  - Monopole suppressed adiabatic potential (Present calculation)
- 4)  $\beta^3 = 1$  - Full adiabatic potential (Present calculation)

FIG. 4.5 d-wave phase shifts ( $e^- - H$ )

a) Singlet      b) Triplet

- 1) E.P. - extended polarization (Callaway et al - 1968)
- 2) AED - exchange adiabatic dipole (Callaway et al - 1968)
- 3)  $\beta^3 = 0$  - Monopole suppressed adiabatic potential (Present calculation)
- 4)  $\beta^3 = 1$  - Full adiabatic potential (Present calculation)

FIG. 5.1 s-wave phase shifts (radians) ( $e^+ - H$ )

- 1)  $\alpha = 1$  Full Dalgarno and Lynn adiabatic potential
- 2)  $\alpha = 0$  Monopole suppressed adiabatic potential
- 3)  $\alpha = 0.1$  Partial monopole suppression of adiabatic potential
- 4)  $\blacktriangle$  Schwartz values.

FIG. 5.2. Total Cross Sections (in the model discussed in chapter 6 below )

(1s-2s) - ( $e^- - H$ ) plotted against the monopole suppression factor  $\beta$  at 1) 0.8 ryd , 2) 1.0 ryd)

FIG. 5.3. S-wave phase shifts for ( $e^- - H$ ) plotted against the monopole suppression factor  $\beta$  at 0.81 ryd 1) singlet, 2) triplet

FIG 5.4. Total Cross Sections - (1s-2s) - ( $e^- - H$ ) Single particle polarization approximation

- 1) Extended polarization approximation
- 2) Exchange adiabatic approximation - dipole only (AED)
- 3) Monopole suppressed (MS)
- 4) Full adiabatic potential (AET)
- X Experimental - Lichten and Schultz (1959)-renormalised to Fite (1968)

FIG. 5.4. cont'd) - 108 -  
 peak  $(0.18 \pi a_0^2)$

FIG. 5.5. Total Cross Sections - (1s-2p) - ( $e^-$ -H) Single particle  
 polarization approximation

- 1) Extended polarization
- 2) Exchange Adiabatic (Monopole Suppressed) - AED not distinguishable on this scale.

FIG. 6.1. Polarised Born Approximation - Total Cross Sections (1s-2s)  
 ( $e^-$ -H)

- 1) Born Approximation
  - 2)  $s = 1, 2$  (dipole and quadrupole polarization)
  - 3)  $s = 0, 1$
  - 4)  $s = 0, 1, 2$
  - 5)  $s = 0, 1, 2$  (Moiseiwitch convention)
- $s = 0, 1, 2, 3$  coincides closely with (5) on this scale

FIG. 6.2. Polarized Born Approximation - Total Cross Sections (1s-2p)  
 ( $e^-$ -H)

- 1) Born Approximation
- 2)  $s = 0, 1$
- 3)  $s = 0, 1, 2$
- 4)  $s = 0, 1, 2, 3$
- 5)  $s = 0, 1, 2, 3$  (Moiseiwitch convention)

$s = 1, 2$  approximation coincides closely with (4) at all energies.

FIG. 6.3. Polarized Born Approximation - differential cross sections  
 (1s-2s) ( $e^-$ -H) at  $k^2 = 1$  ryd.

- 1) Born Approximation
- 2)  $s = 0, 1$
- 3)  $s = 0, 1, 2, 3$



FIG. 6.3. (Cont'd)

5)  $s = 0, 1, 2, 3$  (Moiseiwitch Convention)

FIG. 6.4. Polarized Born Approximation - Differential cross sections

(1s-2p) ( $e^-$  - H) at  $k^2 = 1$  ryd

1) Born Approximation

2)  $s = 0, 1$

4)  $s = 0, 1, 2, 3$

5)  $s = 0, 1, 2, 3$  (Moiseiwitch Convention)

PARTIAL CROSS SECTIONS - Single particle polarization approximation

(1s-2s) ( $e^-$  - H)

6.6. Triplet s-wave

6.7. Triplet p-wave

6.8. Singlet s-wave

6.9. Singlet p-wave

6.10. Singlet d-wave

2) 3-state close coupling (1s-2s-2p)

3) 6-state close coupling (1s-2s-2s-3s-3p-3d)

1) Extended polarization approximation

4) Central field Exchange approximation

PARTIAL CROSS SECTIONS - Single Particle polarization approximation (1s-2p)

( $e^-$  - H)

6.11. Triplet s-wave

6.12. Triplet p-wave

6.13. Singlet s-wave

6.14. Singlet p-wave

6.15. Singlet d-wave

1) extended polarisation approximation;

4) central field exchange approximation;

5) full polarisation (direct).

6.20 TOTAL CROSS SECTIONS - Single particle polarization approximation

(1s-2s) ( $e^-$  - H)

- 1) Born approximation
- 2) Extend Polarization approximation
- 3) 6-state close coupling (1s-2s-2p-3s-3p-3d)
- 4) 3-state close coupling (1s-2s-2p)
- 5) Central field exchange approximation
- 6) Experimental - Lichten and Schultz (1959) renormalised to Fite (1968)  
peak ( $0.18 \pi a_0^2$ )
- 7) Full polarization approximation (direct)

6.21 TOTAL CROSS SECTIONS - Single particle polarization approximation

(1s-2p) ( $e^-$  - H)

- 1) Born approximation
- 2) Central Field exchange approximation
- 3) Extended polarization approximation
- 4) 3- state close coupling (1s-2s-2p)
- 5) 6-state close coupling (1s-2s-2p-3s-3p-3d)
- 6) Full polarization approximation (direct)

X Experimental results of Chamberlain et al (1964)

6.22 TOTAL CROSS SECTIONS - (1s-2s) - ( $e^-$  - H)

- 1) Full polarization approximation (direct)
- 2) Full polarization approximation (direct and exchange)
- 3) Polarized Born Oppenheimer (direct)
- 4) Symmetrised Born approximation.

6.23 TOTAL CROSS SECTIONS - (1s-2p) - ( $e^-$  - H)

- 1) Full polarization approximation (direct)
- 2) Polarized Born Oppenheimer (direct)
- 3) Symmetrised Born approximation.

6.24 TOTAL CROSS SECTION ( $e^- - H$ ) (1s-2s)

- 1) Extended polarization approximation.
- 2) Born Approximation
- 3) Experiment Hils et al (1966)

6.25 CROSS SECTIONS ( $e^- - H$ ) (1s-2s)

Extended Polarization Approximation (present calculation)

- 1) Total singlet cross sections.
- 2) Triplet d-wave partial cross section (multiplied by a spin weighting factor of 3.0).

FIG 0.1

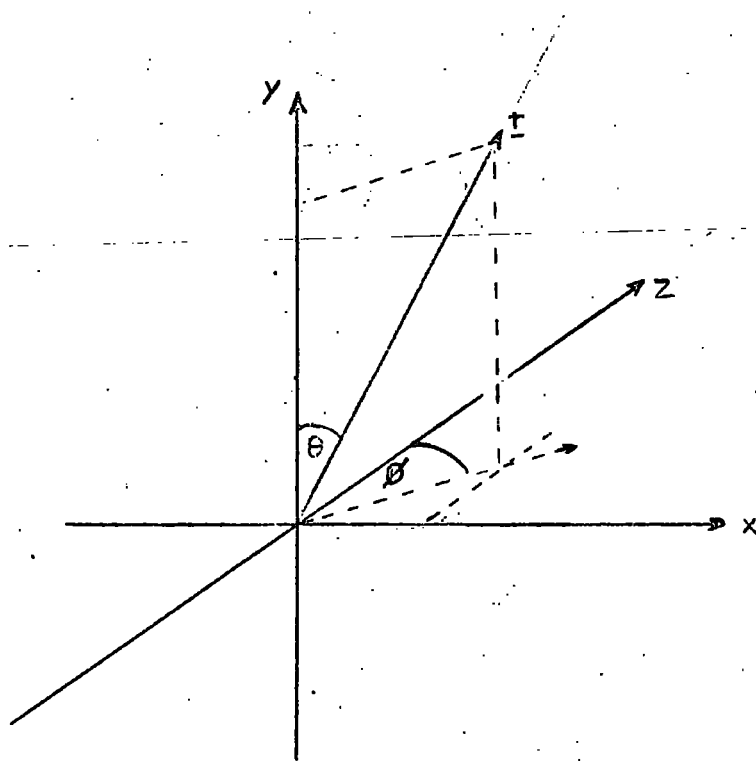
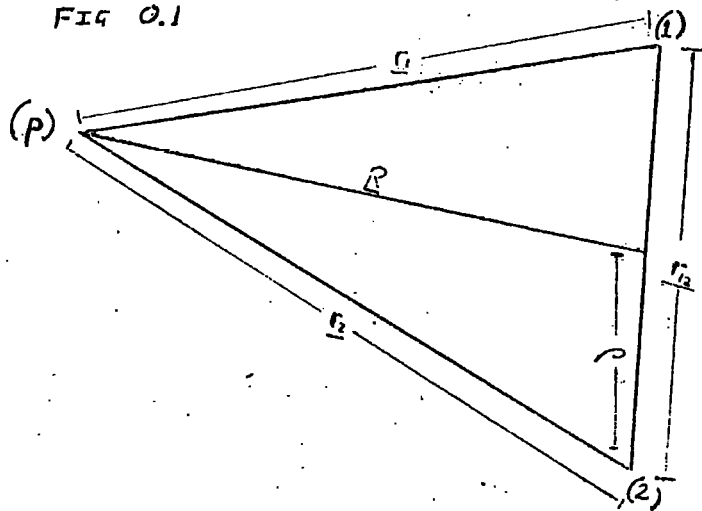


Fig 1.1  $e^- - H$  P-wave phase shifts

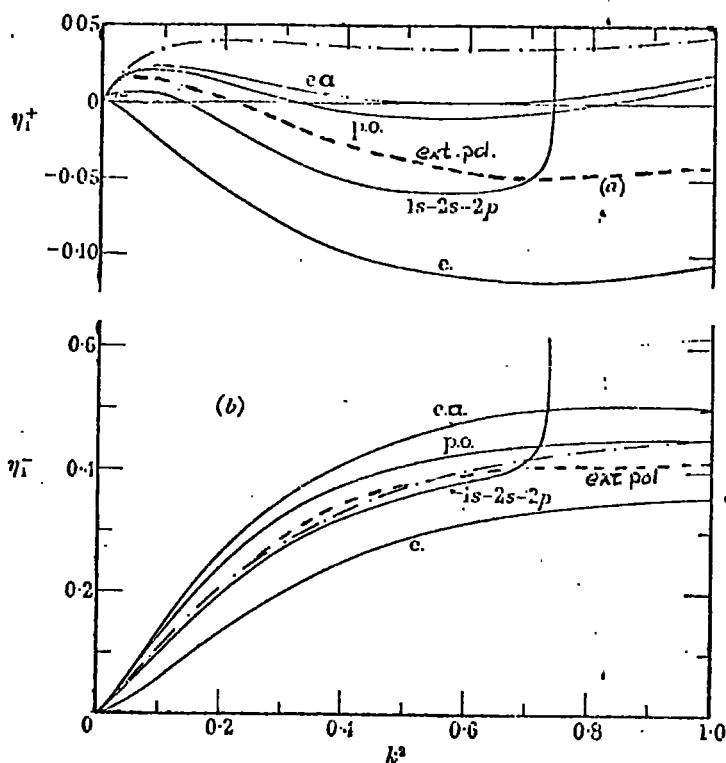


Fig 1.2  $e^- - H$  phase shifts (s-wave)

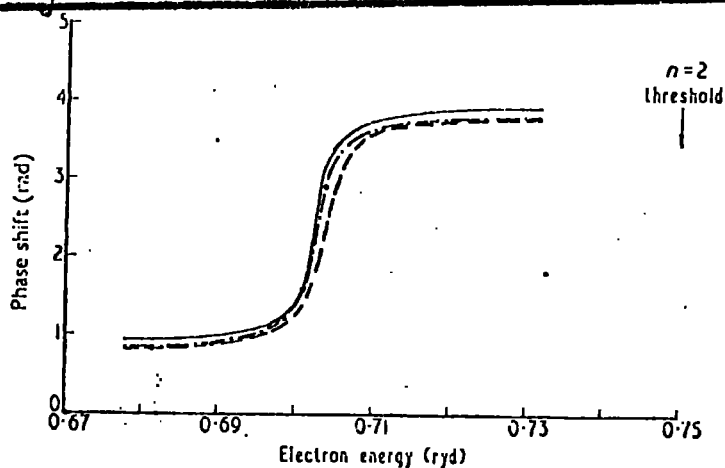


FIG 1.3 MOMENTUM TRANSFER CROSS SECTIONS  $\sigma_m / a_0^2$

ELECTRON - HELIUM

CROMPTON, ELFORD AND JORY  
(EXPERIMENTAL)

EP

AED

AET

0.05 0.1 0.5 1.0 5.0  
 $E \rightarrow (eV)$

Fig 1.4

ELECTRON - HELIUM

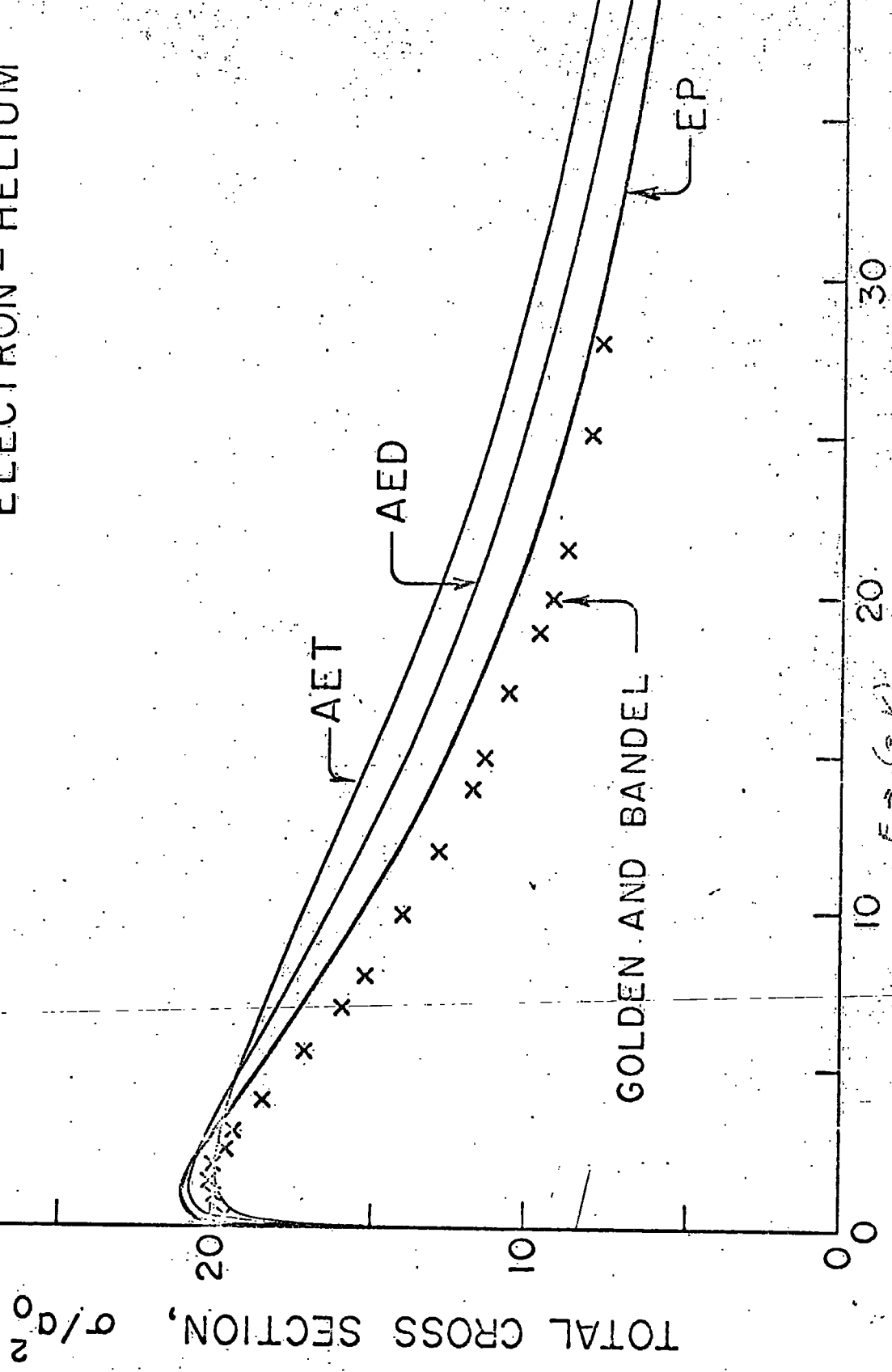


Fig 1.5  $e^-$ -H elastic cross sections

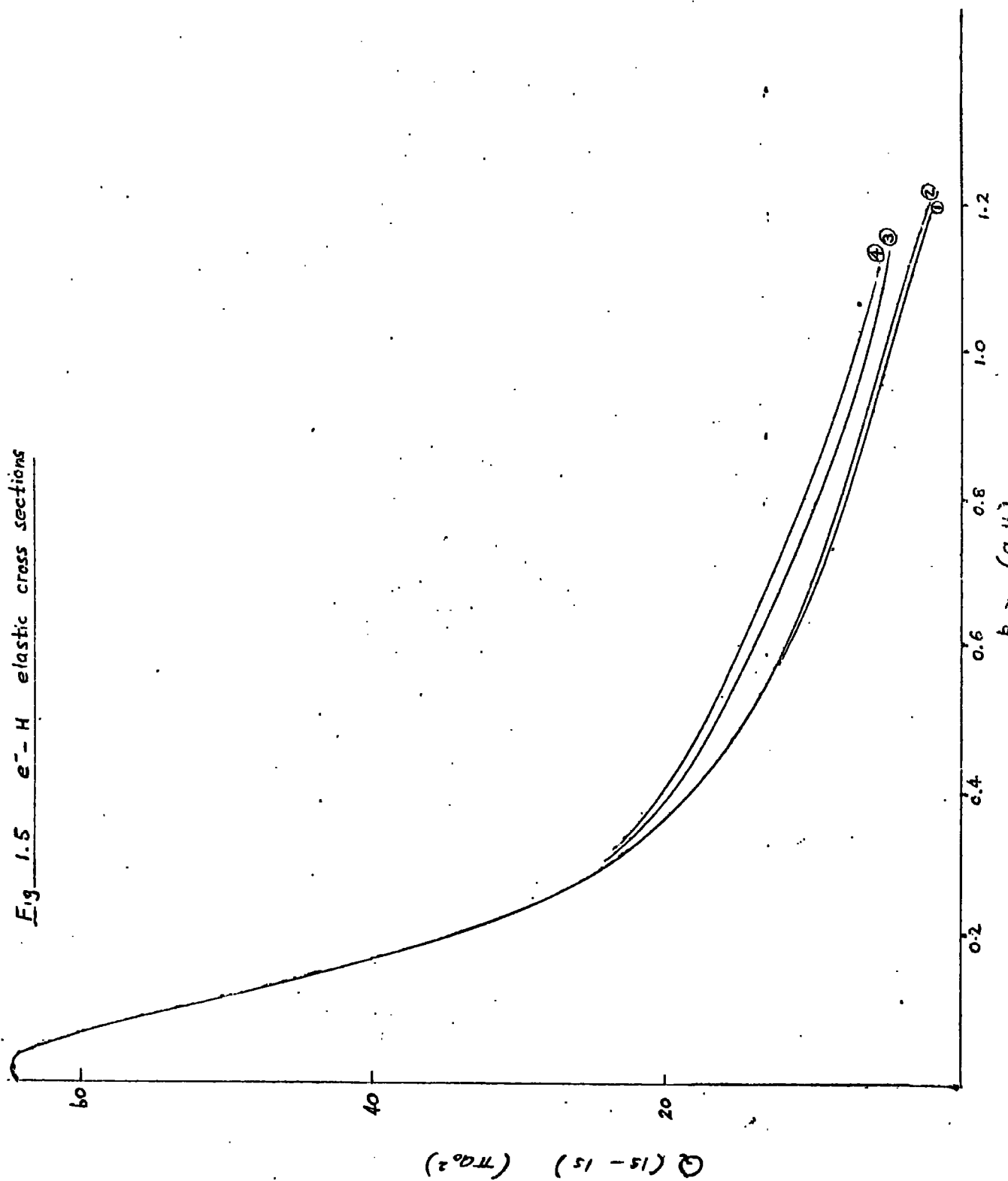




Fig 2.1 (e-H) Singlet & Triplet Cross Section

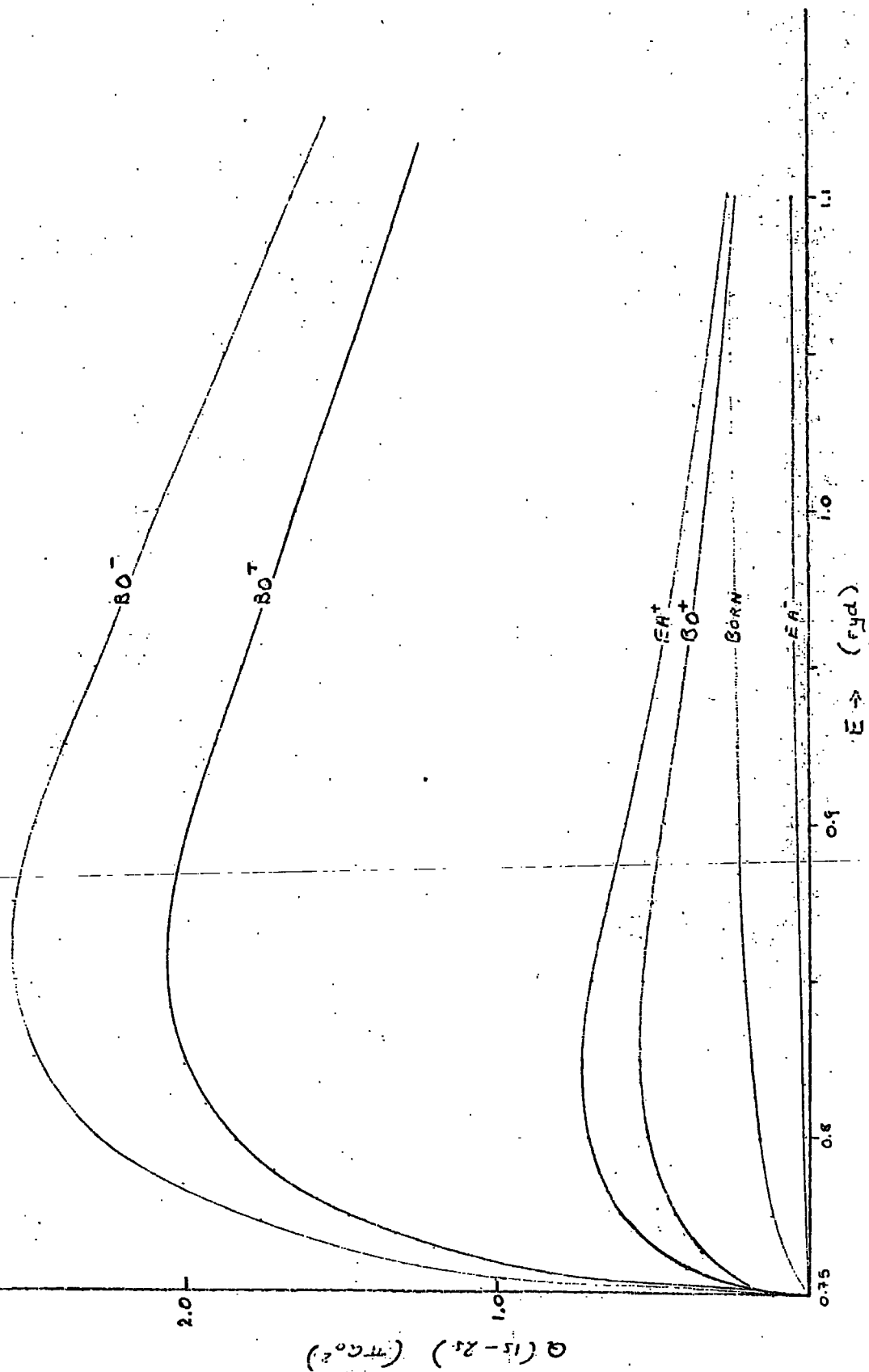
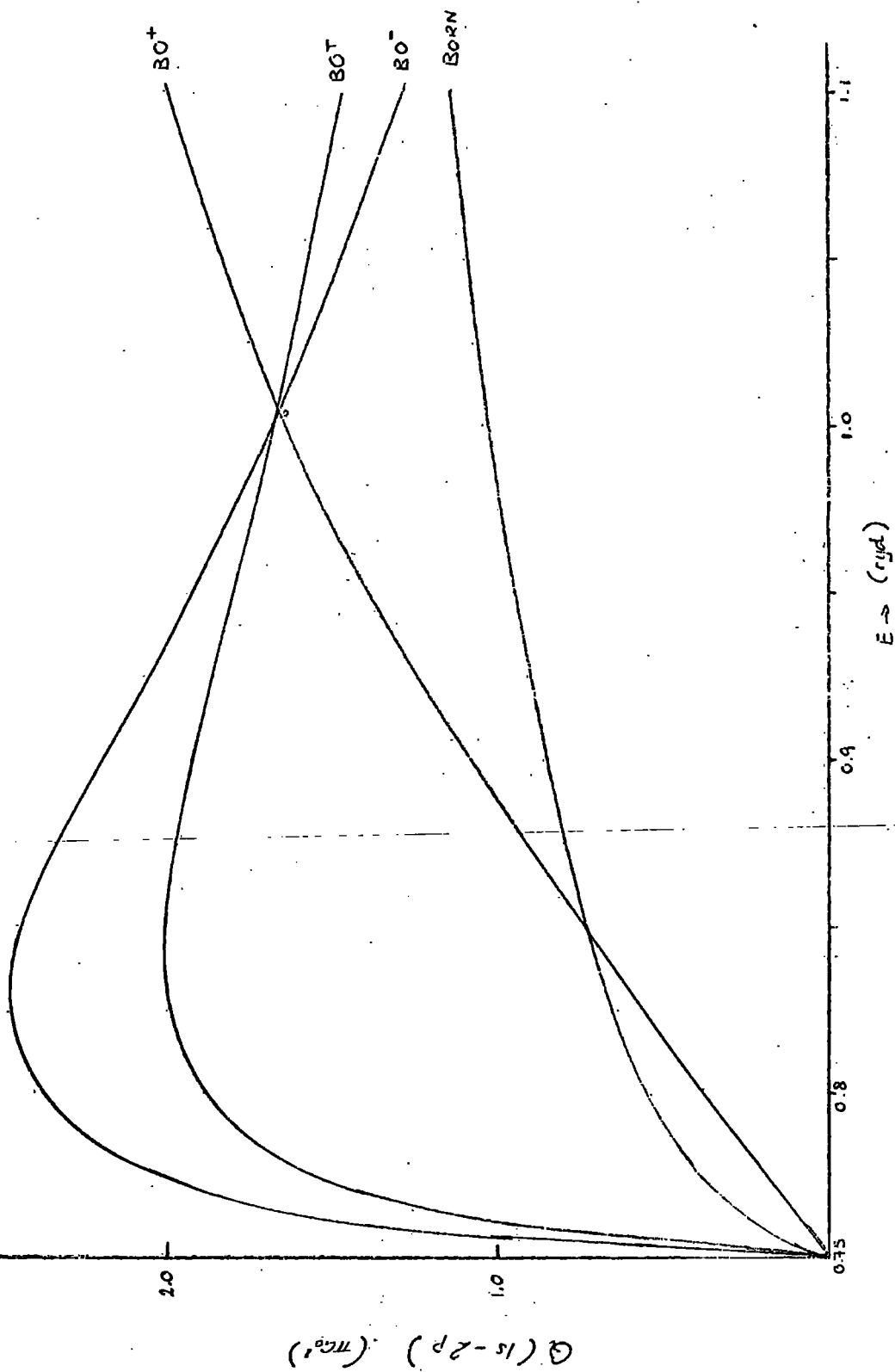


Fig 2.2  $e^- - H$  1s-2p Total Cross Section



2.4  
- H

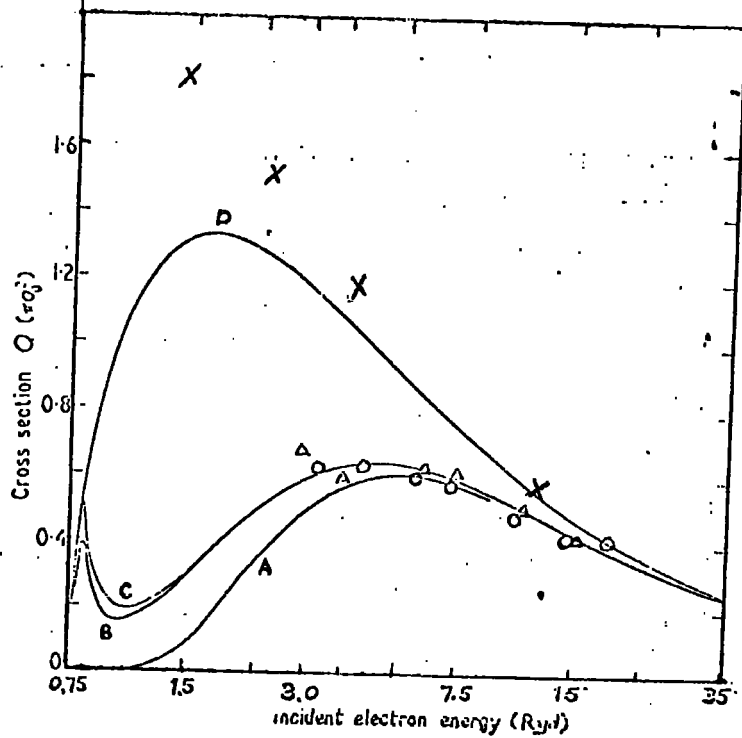


Fig 2.3  
 $e^- - H$

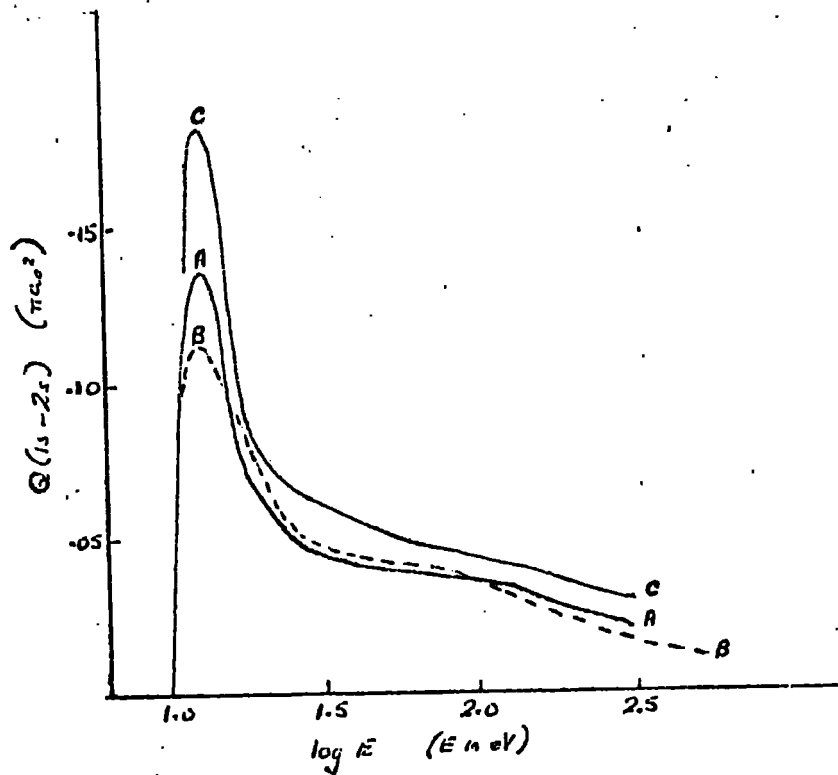


Fig. 2.6  $e^- - H$

Total Cross Sections

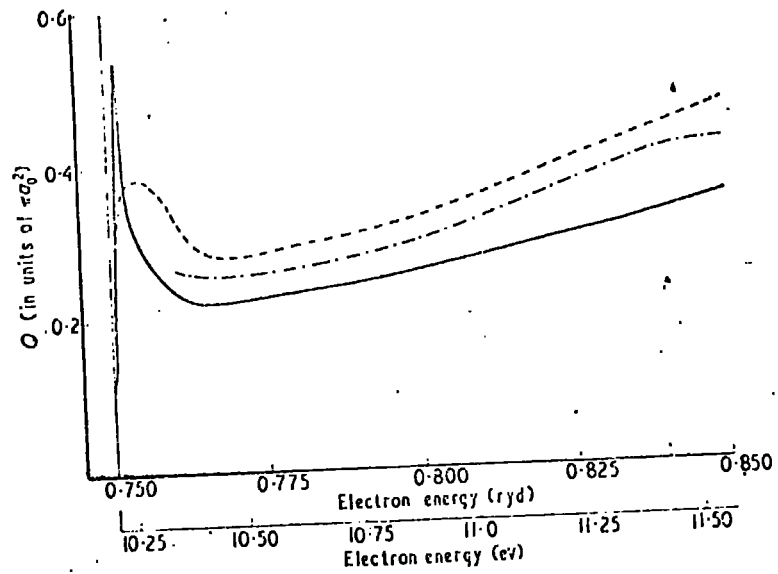
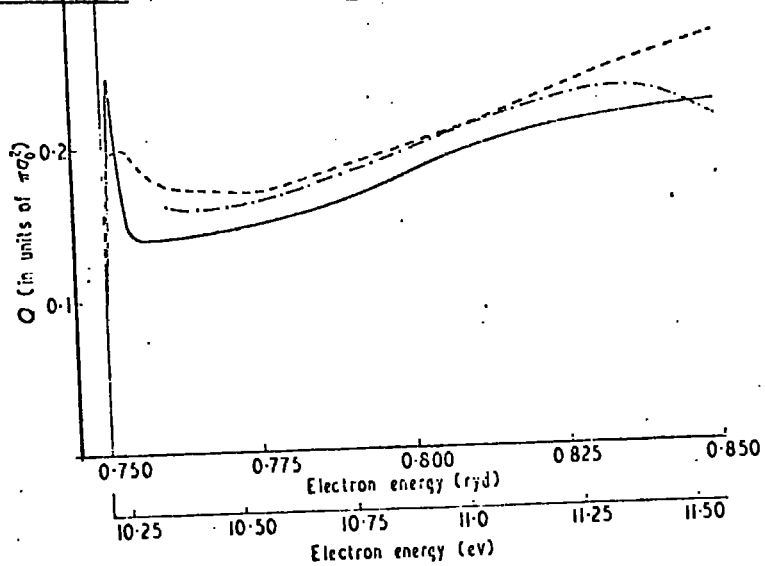


Fig. 2.5  $e^- - H$

Total Cross Sections



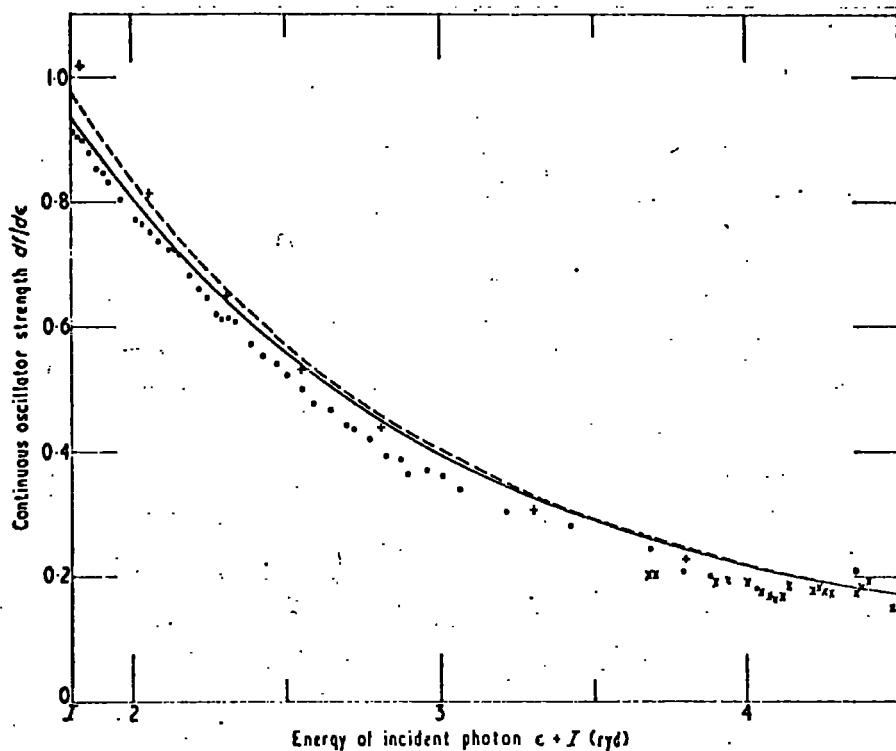


Figure 2.7 Continuous oscillator strength  $df/de$ , calculated with 20-parameter ground-state function and polarized-orbitals free-state function. — dipole length formulation; --- dipole velocity formulation. ● Experimental measurement by Samson (1966); + and × Lowry *et al.* 1965.

Fig 3.1 Total Cross Section (1s-2s) ( $e^- - H$ )

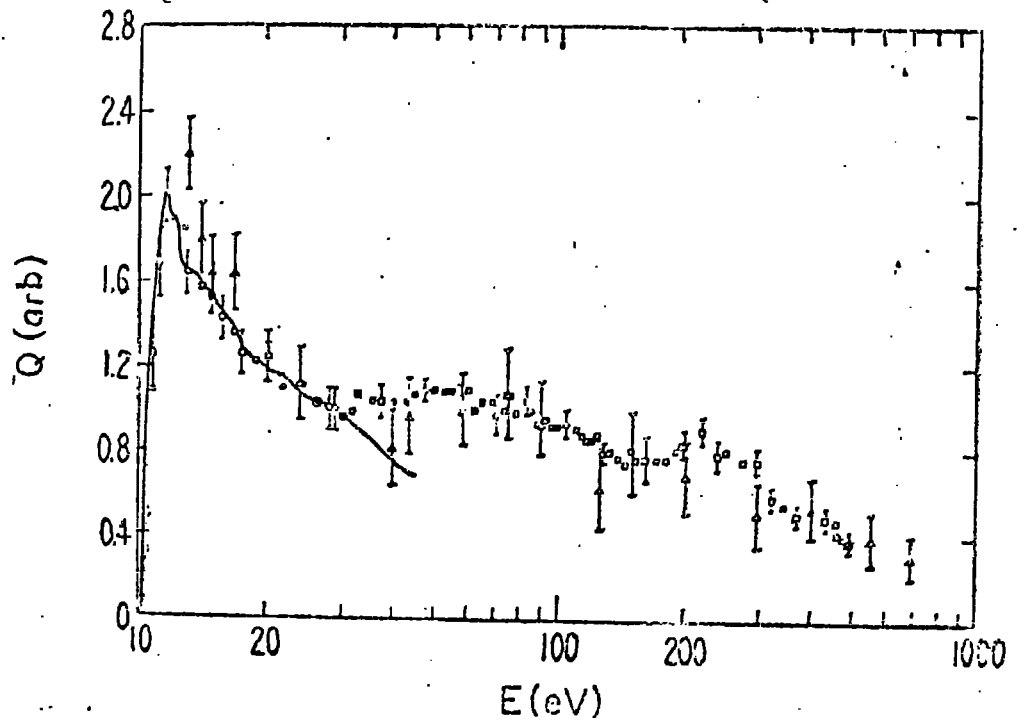
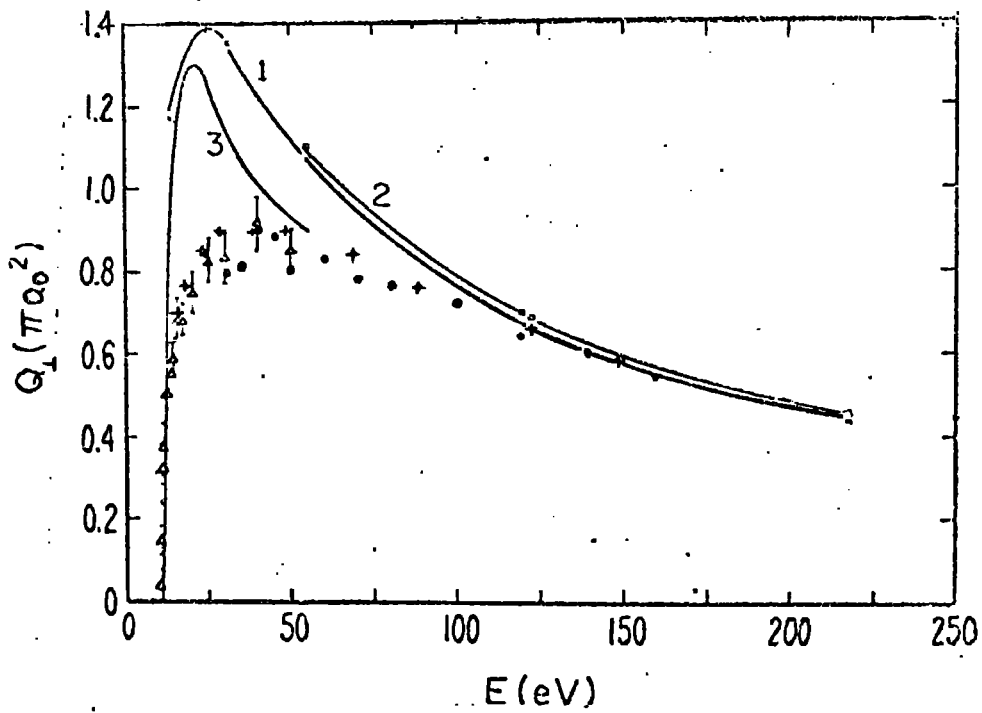


Fig 3.4 Total Cross Section (1s-2p) ( $e^- - H$ )



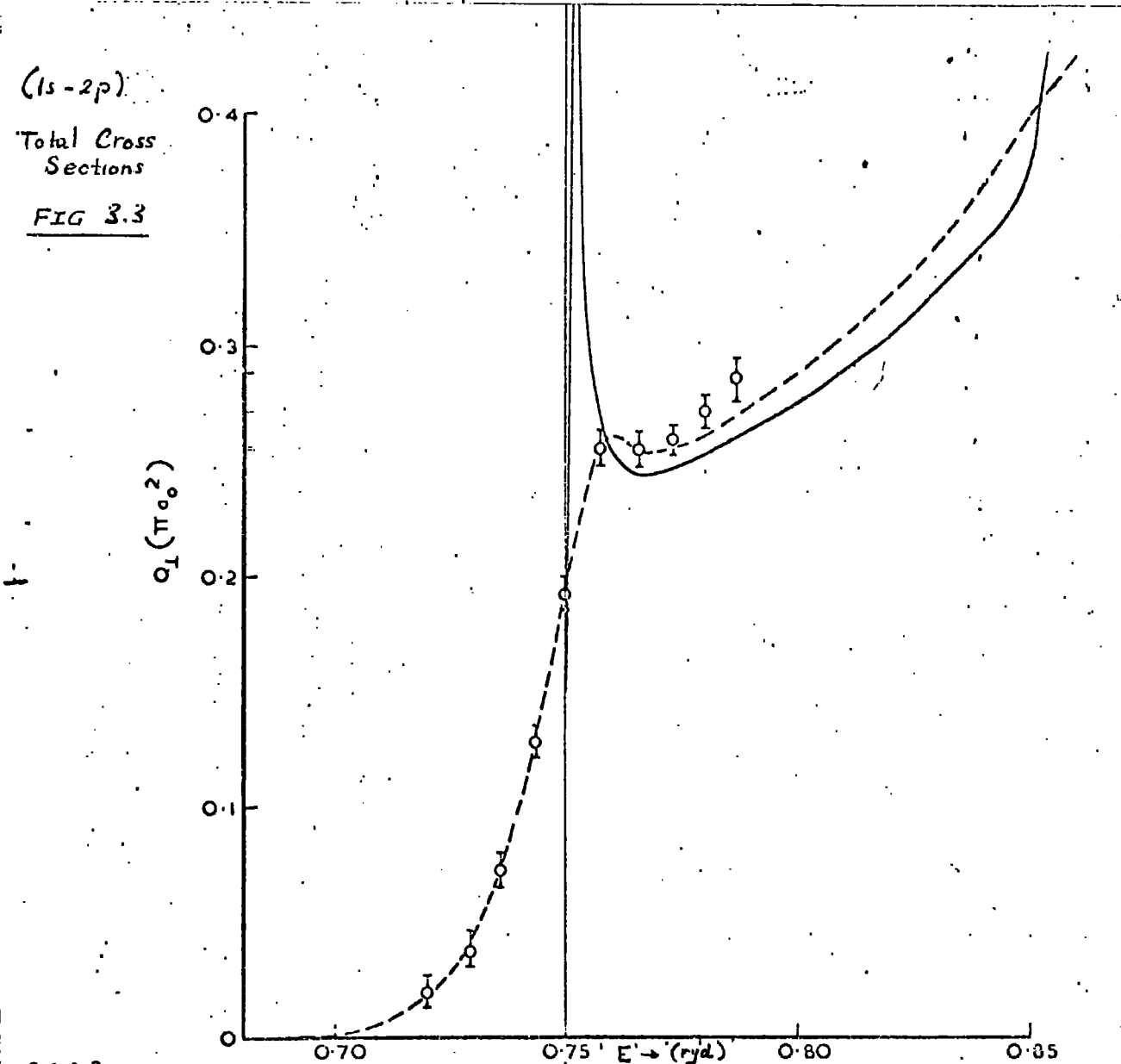
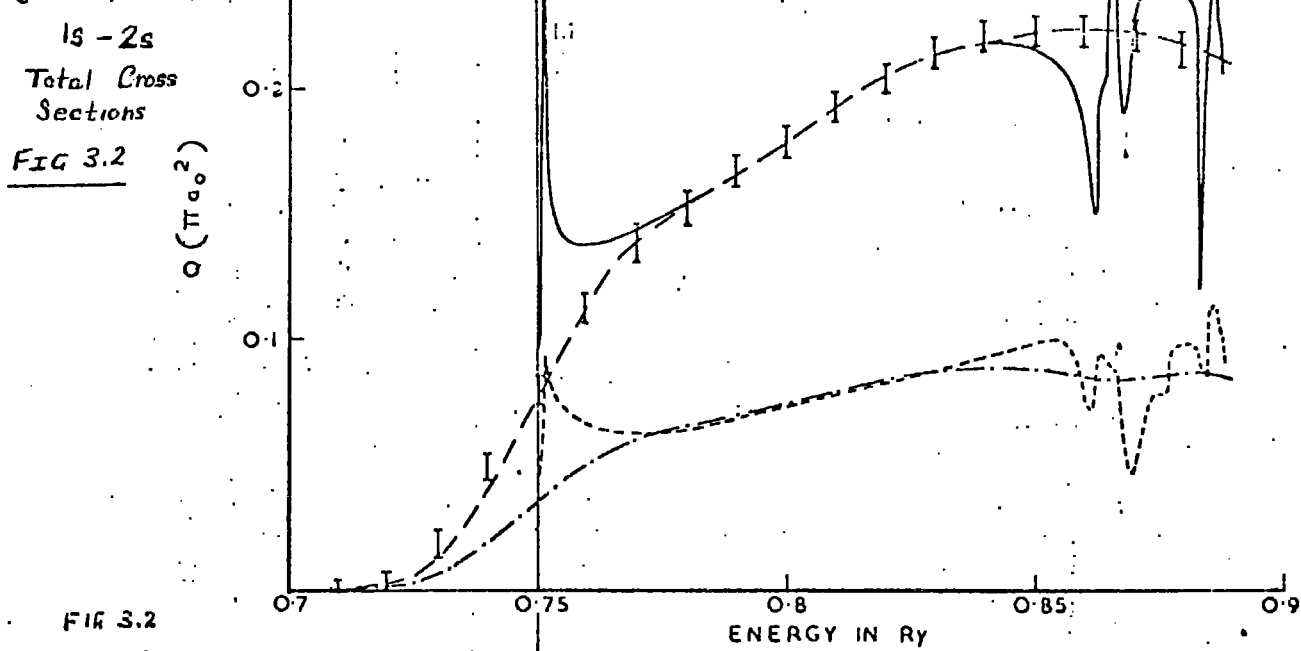
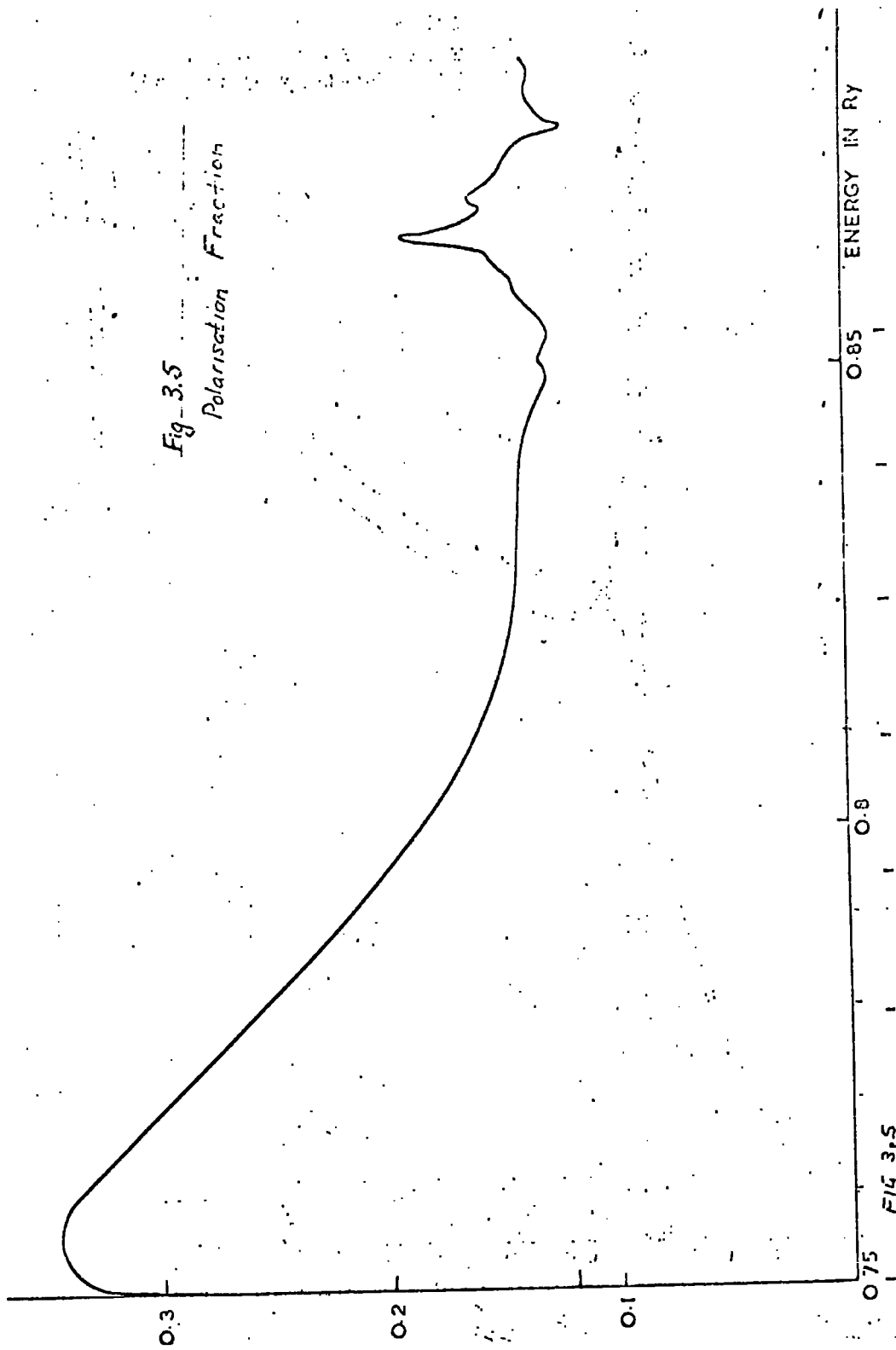


Fig-3.5  
Polarisation Fraction





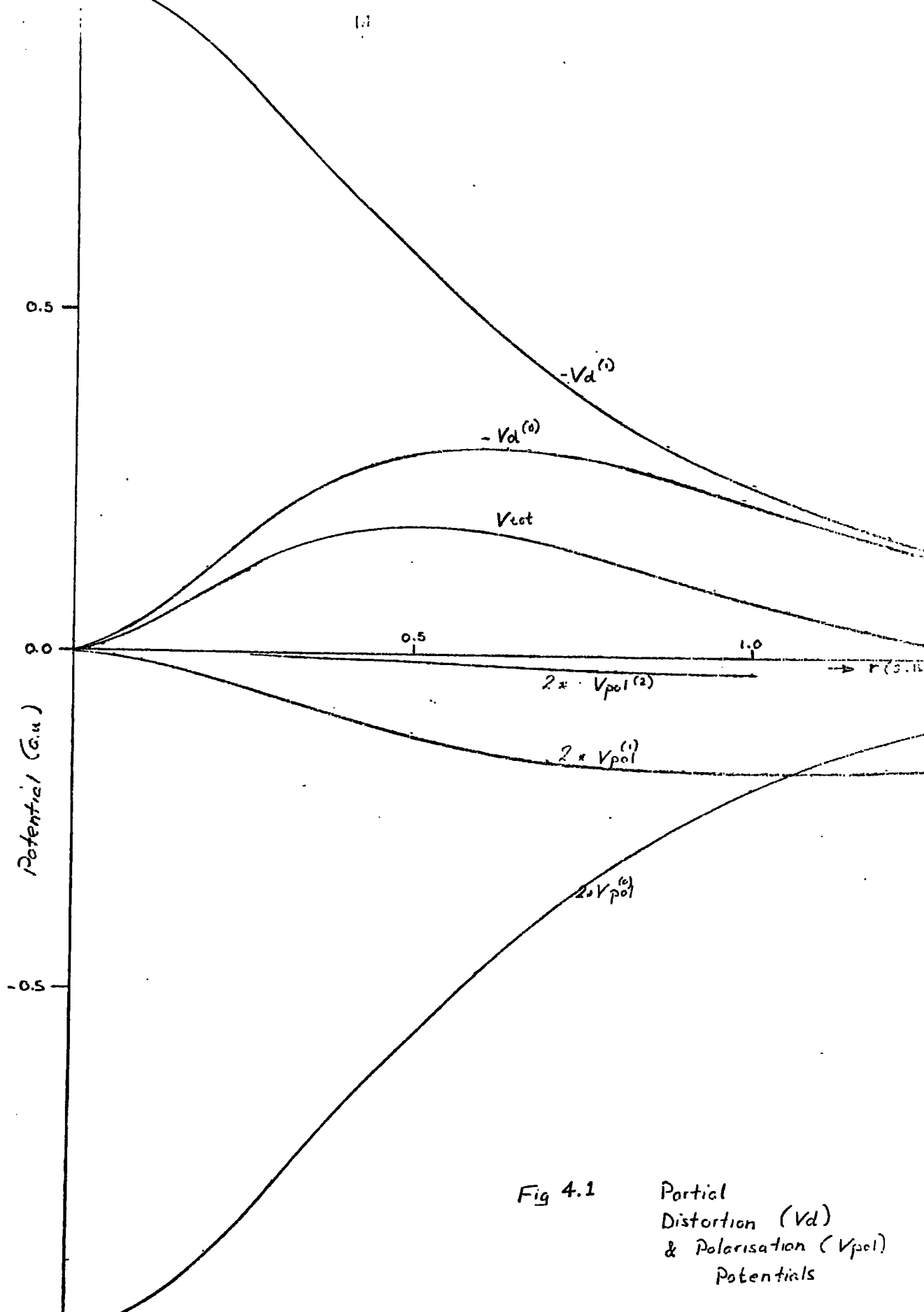


Fig 4.1

Partial  
Distortion ( $V_d$ )  
& Polarisation ( $V_{pol}$ )  
Potentials

Fig. 4.2 Total,  
Distortion  
& Polarisation  
Potentials

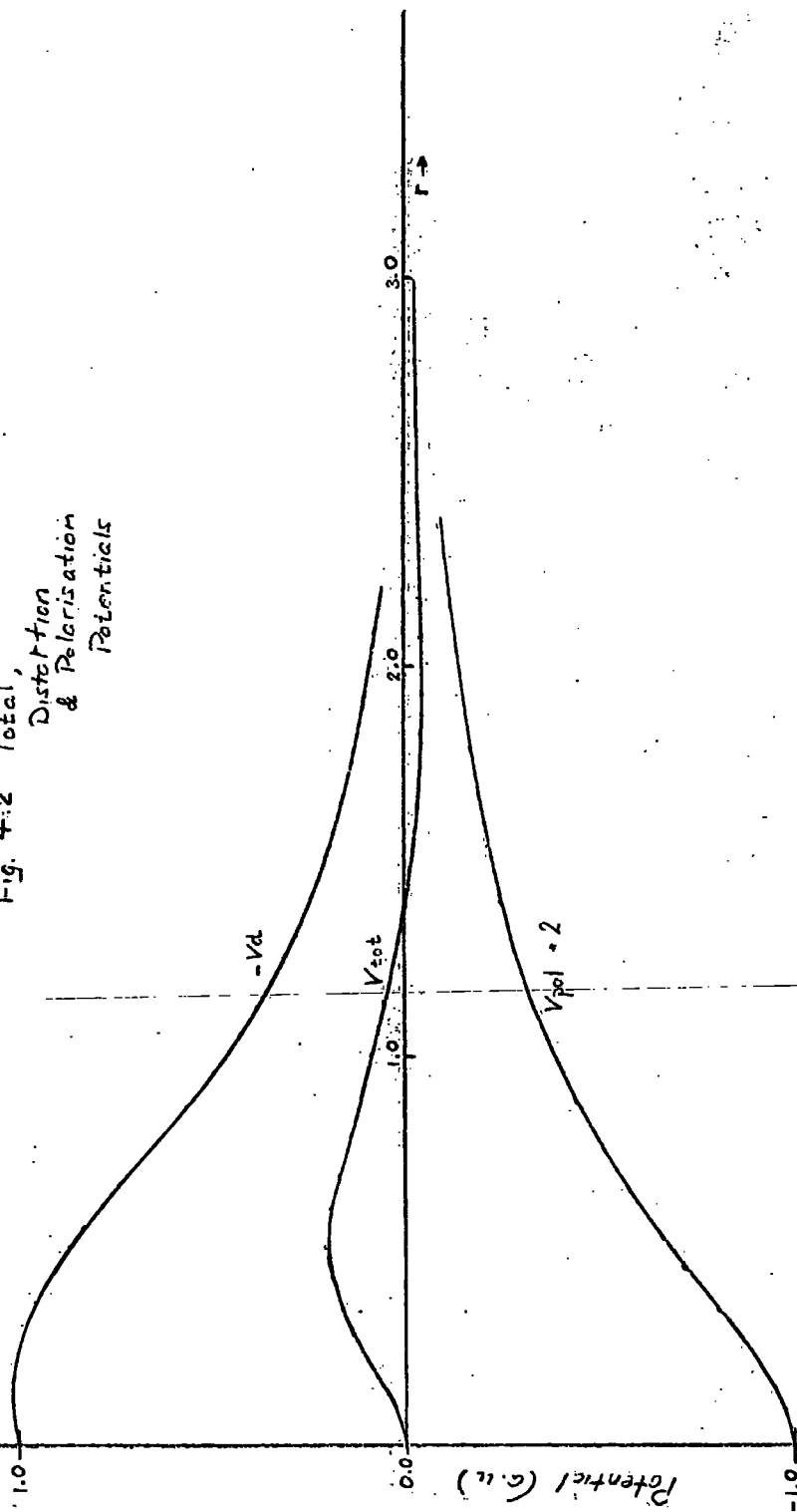
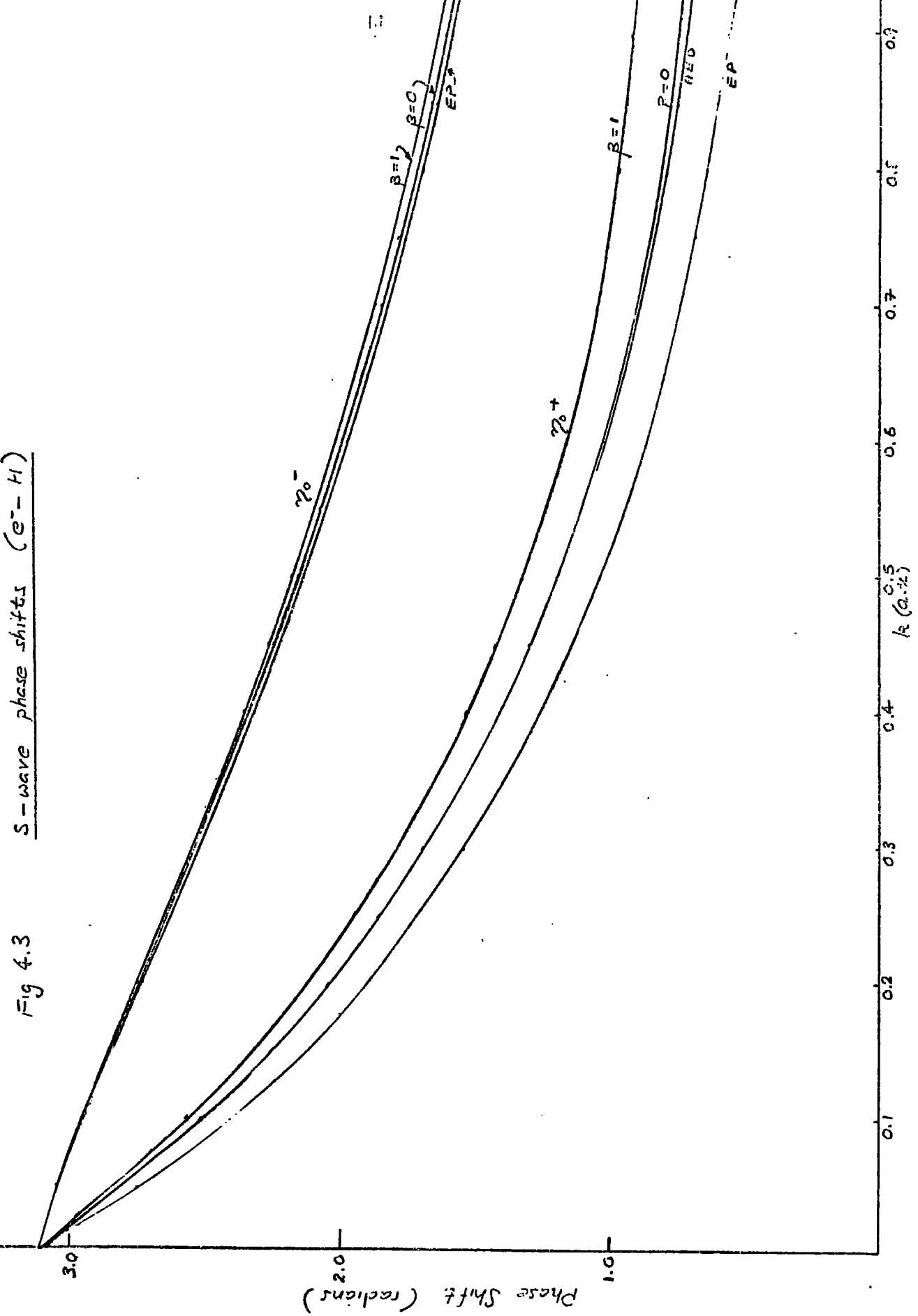


Fig 4.3 S-wave phase shifts ( $e^- - H$ )



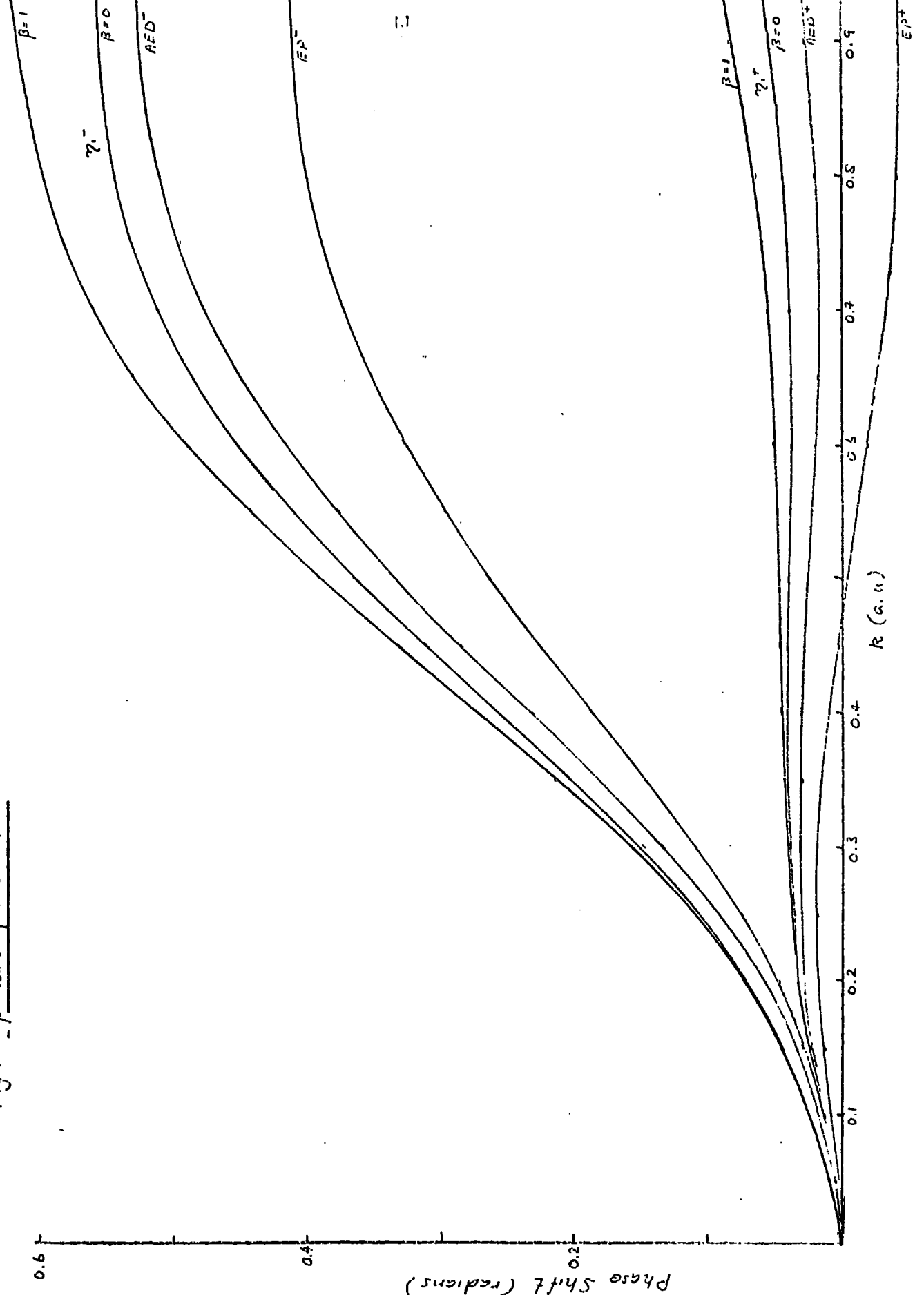


Fig 4.5 d-wave phase shifts ( $0^\circ - 11^\circ$ )

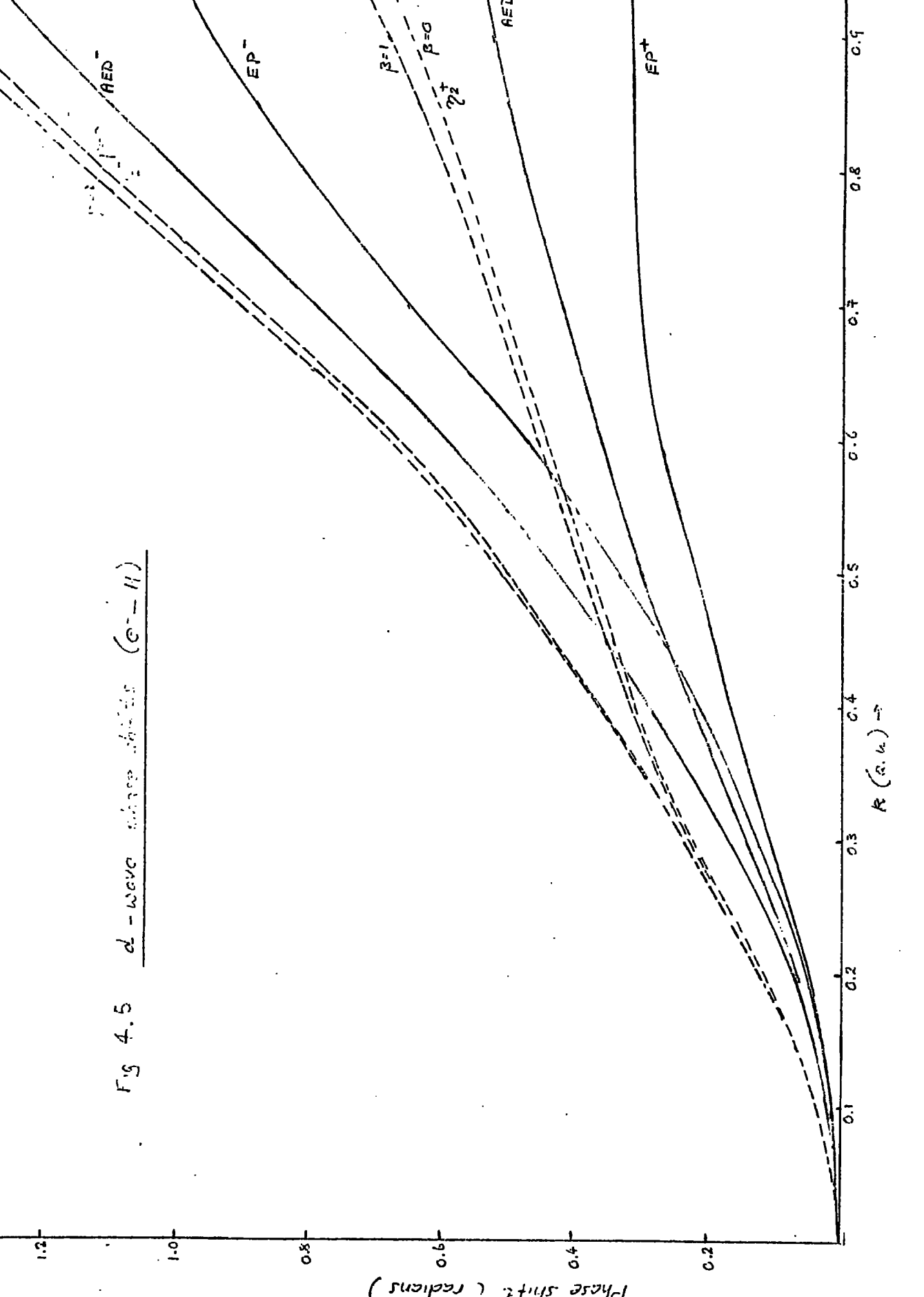


Fig 5.1 S-wave phase shift ( $\delta^+ - 11$ )

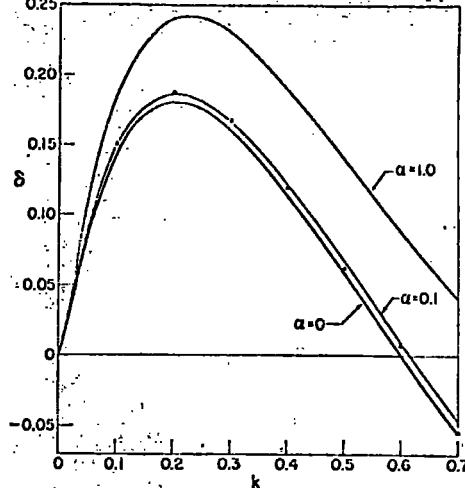
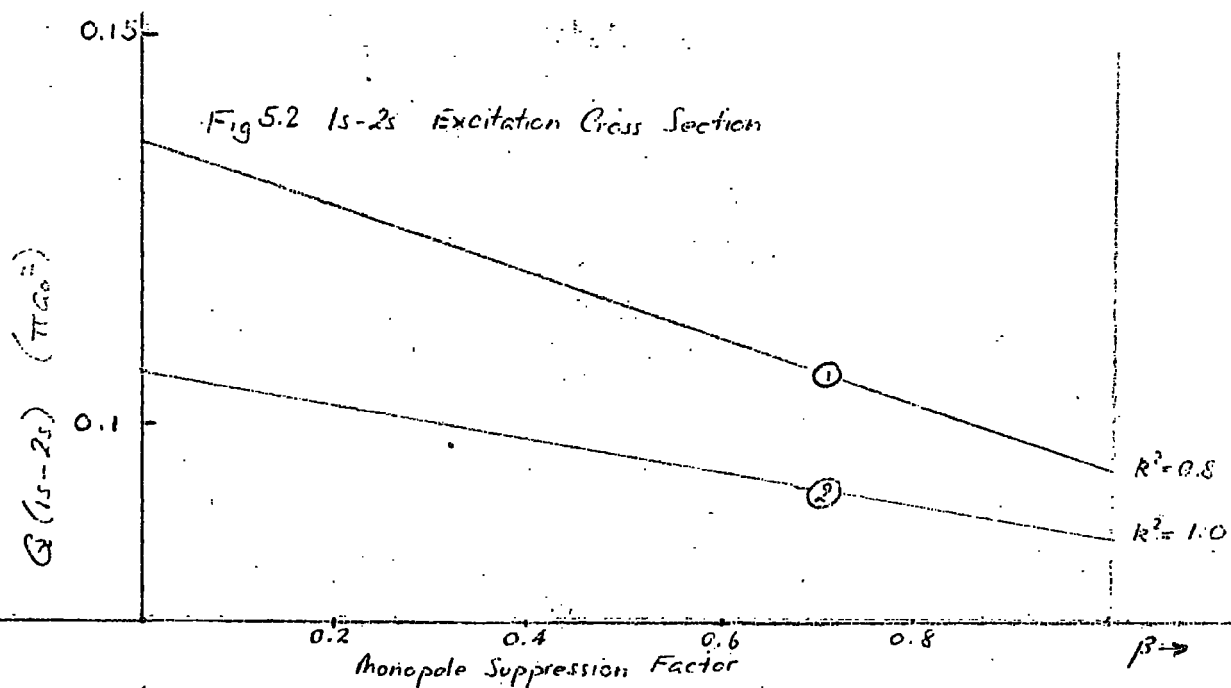


Fig 5.2 1s-2s Excitation Cross Section



$k^2 = 0.81$  s-wave phase shifts

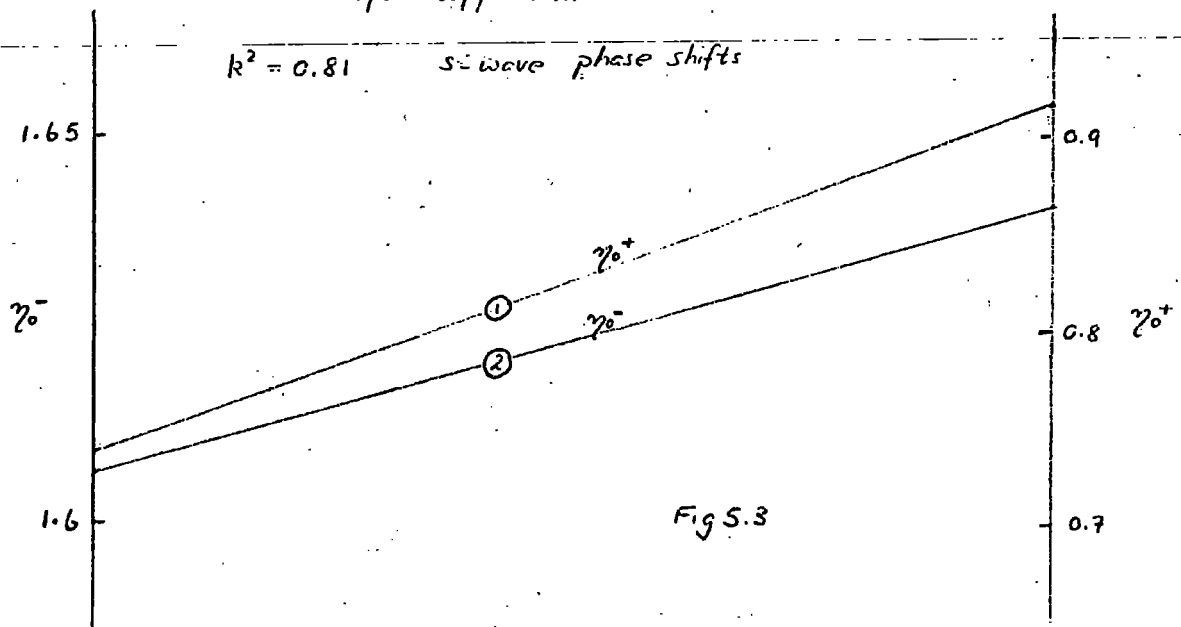


Fig 5.3

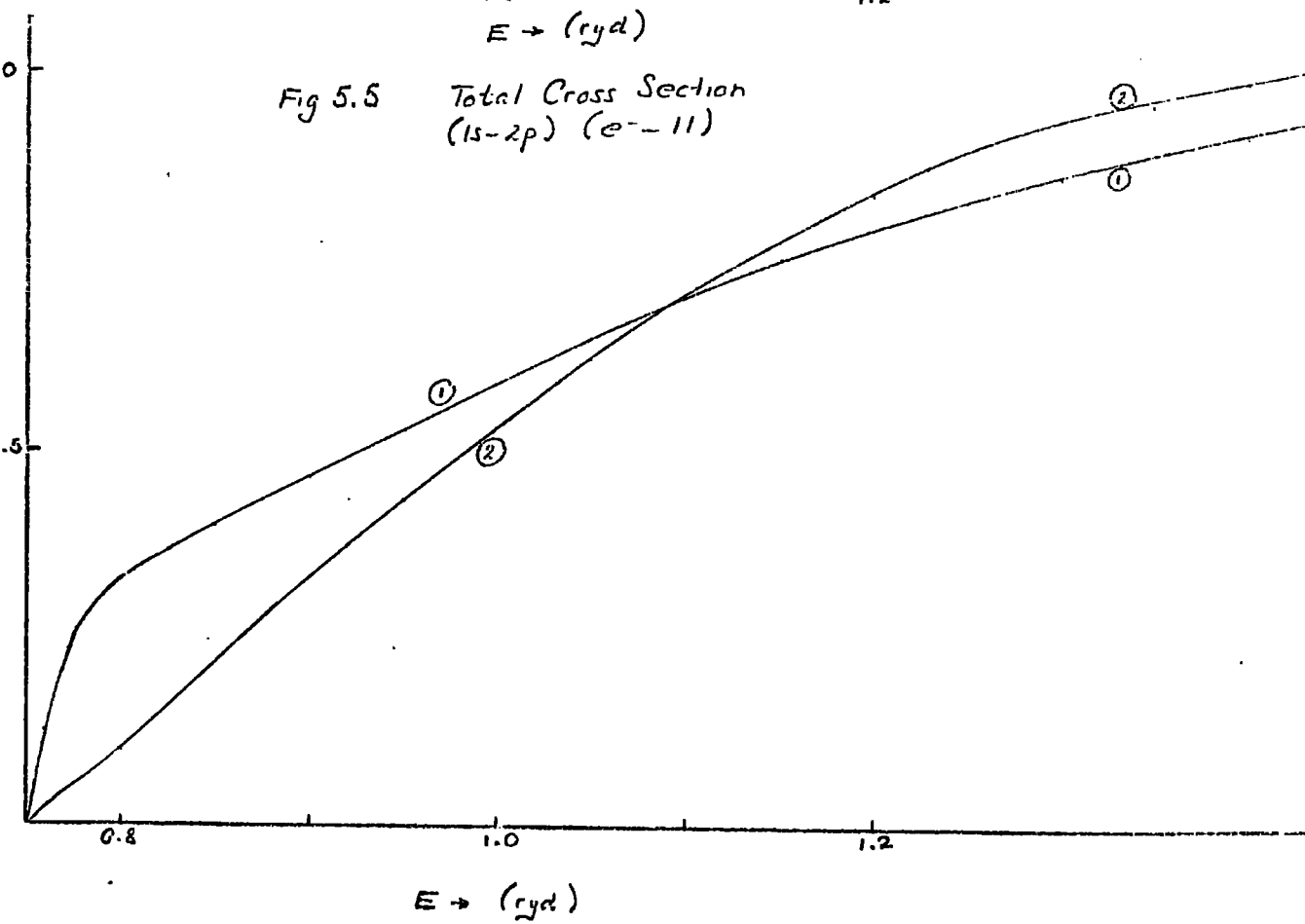
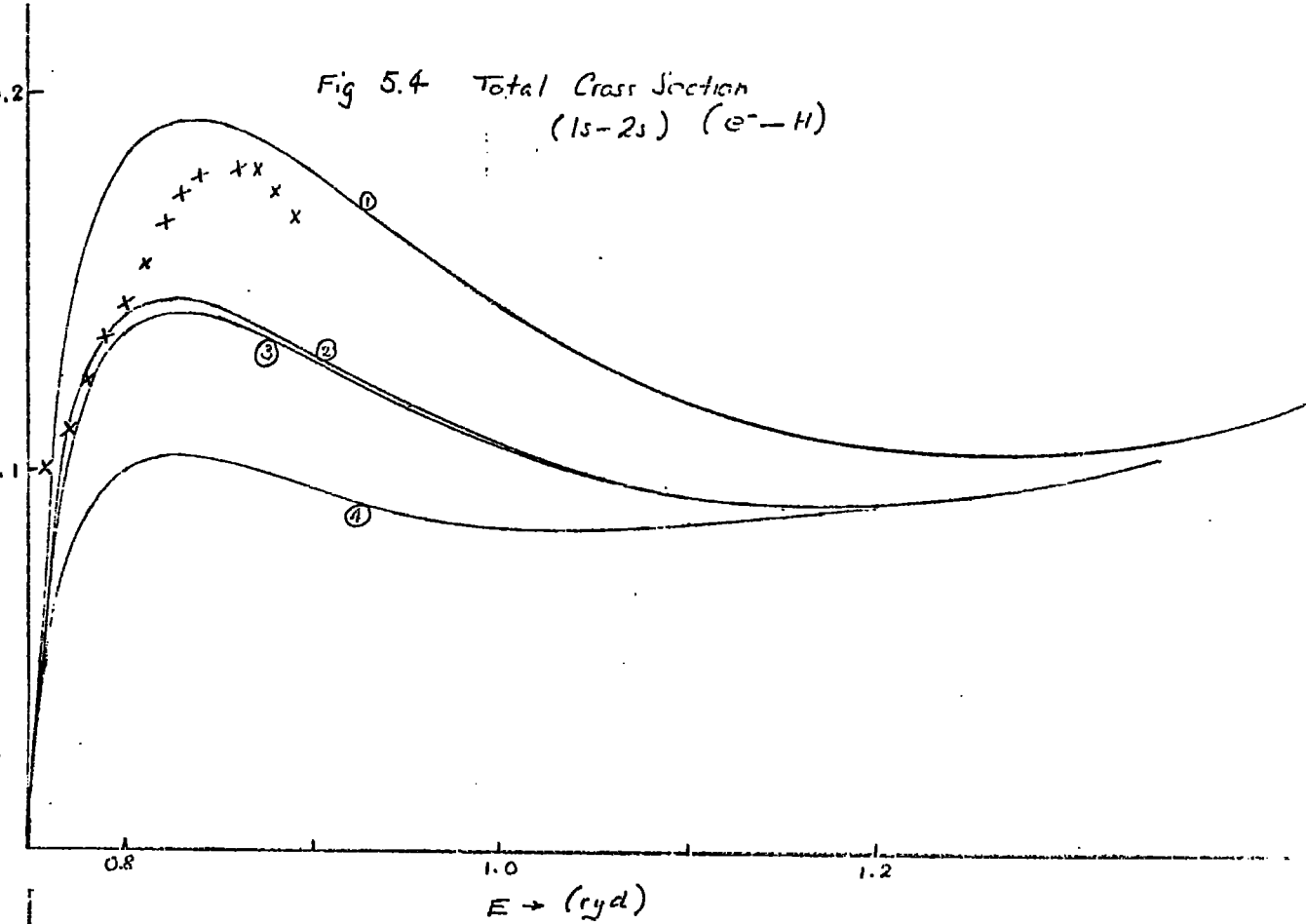


Fig 6.1 1s - 2s Total Cross Section ( $e^- - H$ ) - Polarised Born

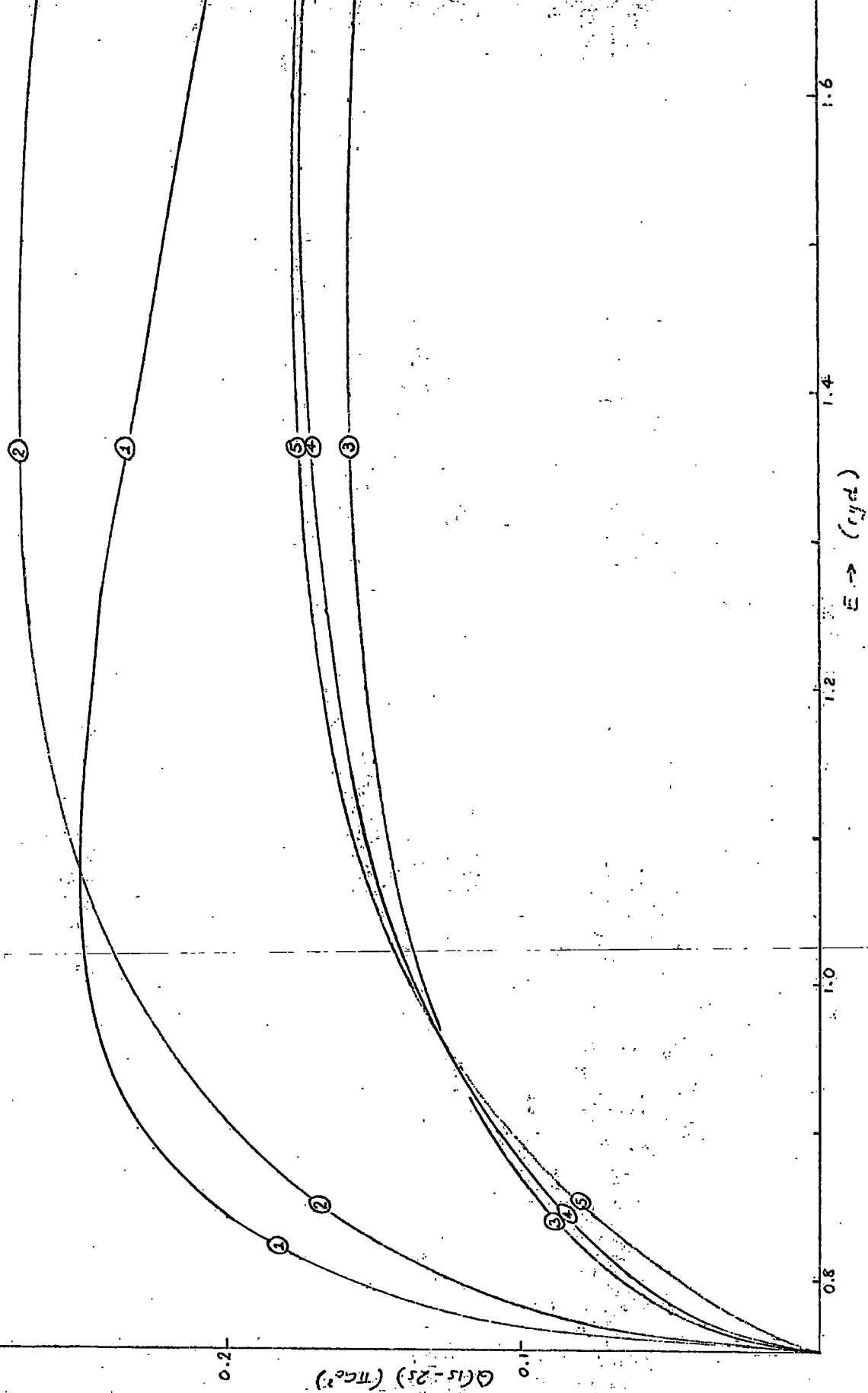




Fig. 6.2 1s-2p Total Cross Section ( $e^- - H$ ) - Polarised Born

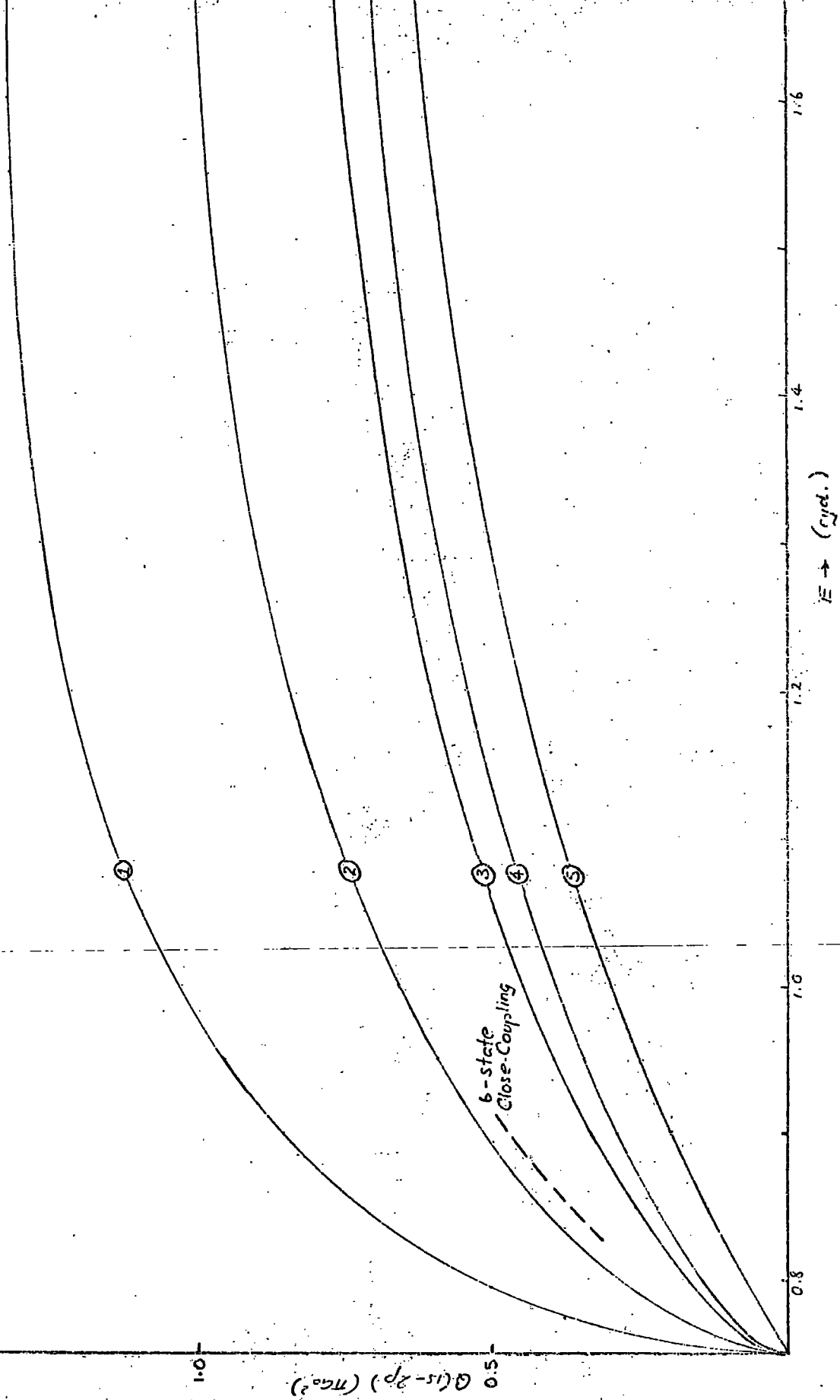


Fig 6.3 Differential Cross Section (1s-2s) ( $e^- - H$ ) at  $E = 1$  ryd.

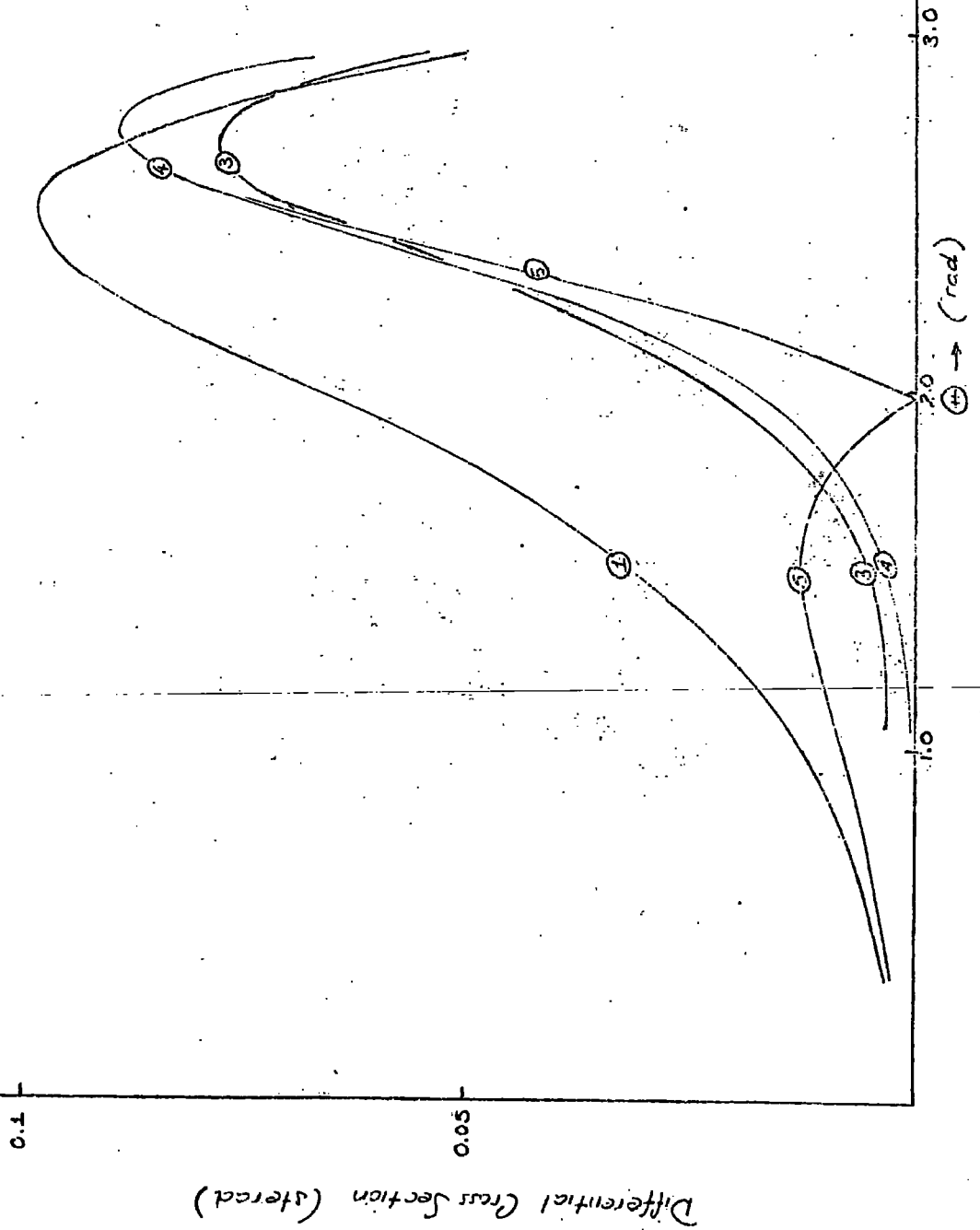


Fig 6.4 Differential Cross Section  
 $(1s-2p) (e-H)$  at  $E=1 \text{ mcd}$

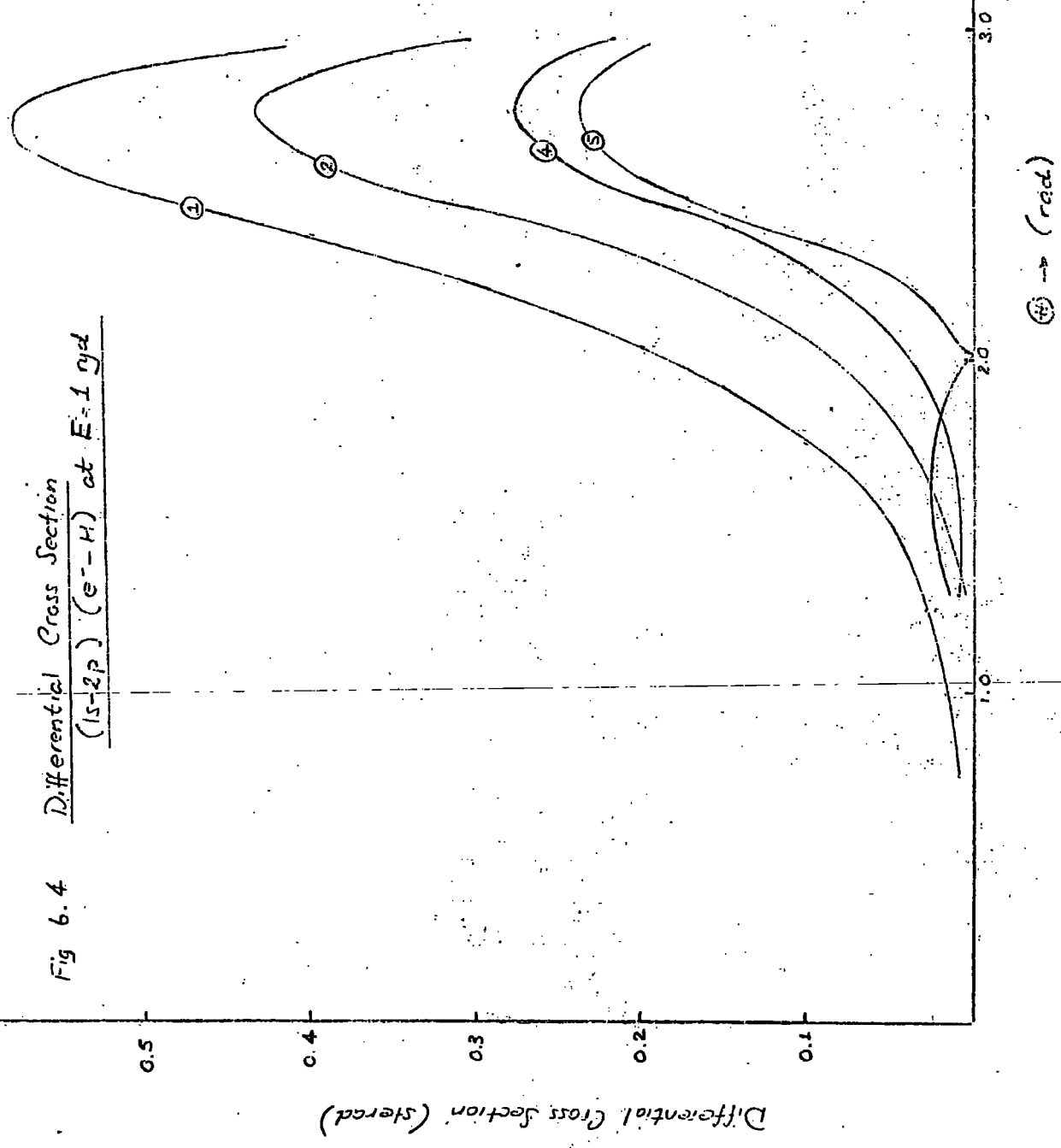


Fig 6.6 Triplet S Partial Cross Section (1s-2s) ( $e^- - H$ )

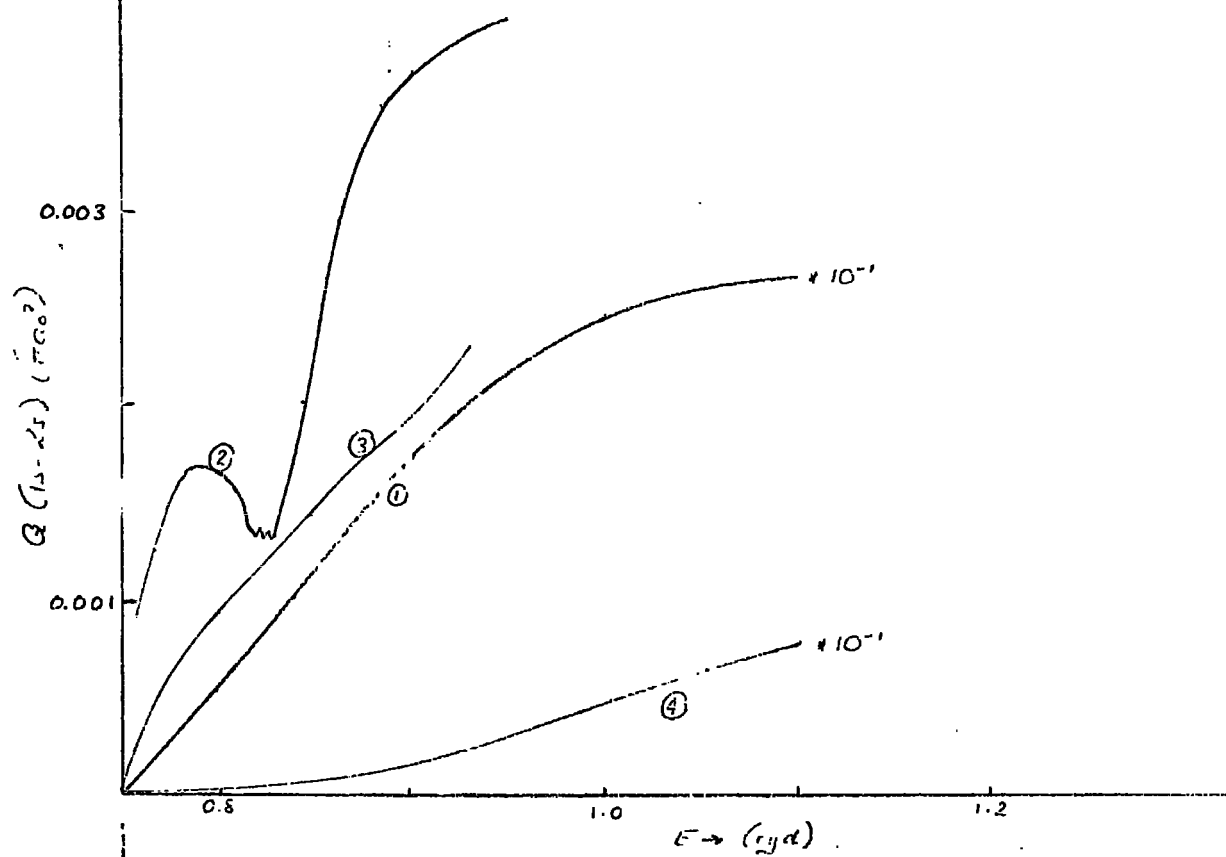
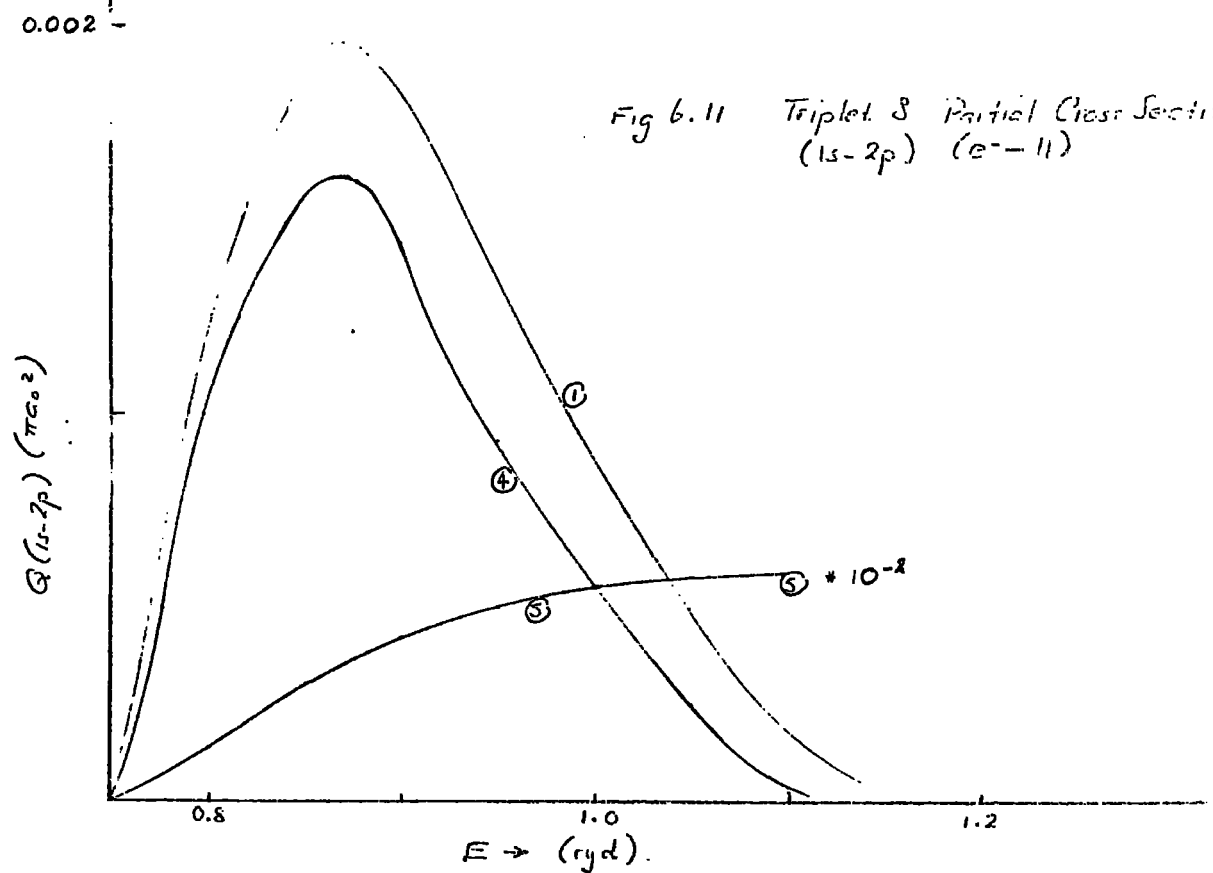


Fig 6.11 Triplet S Partial Cross Section (1s-2p) ( $e^- - H$ )



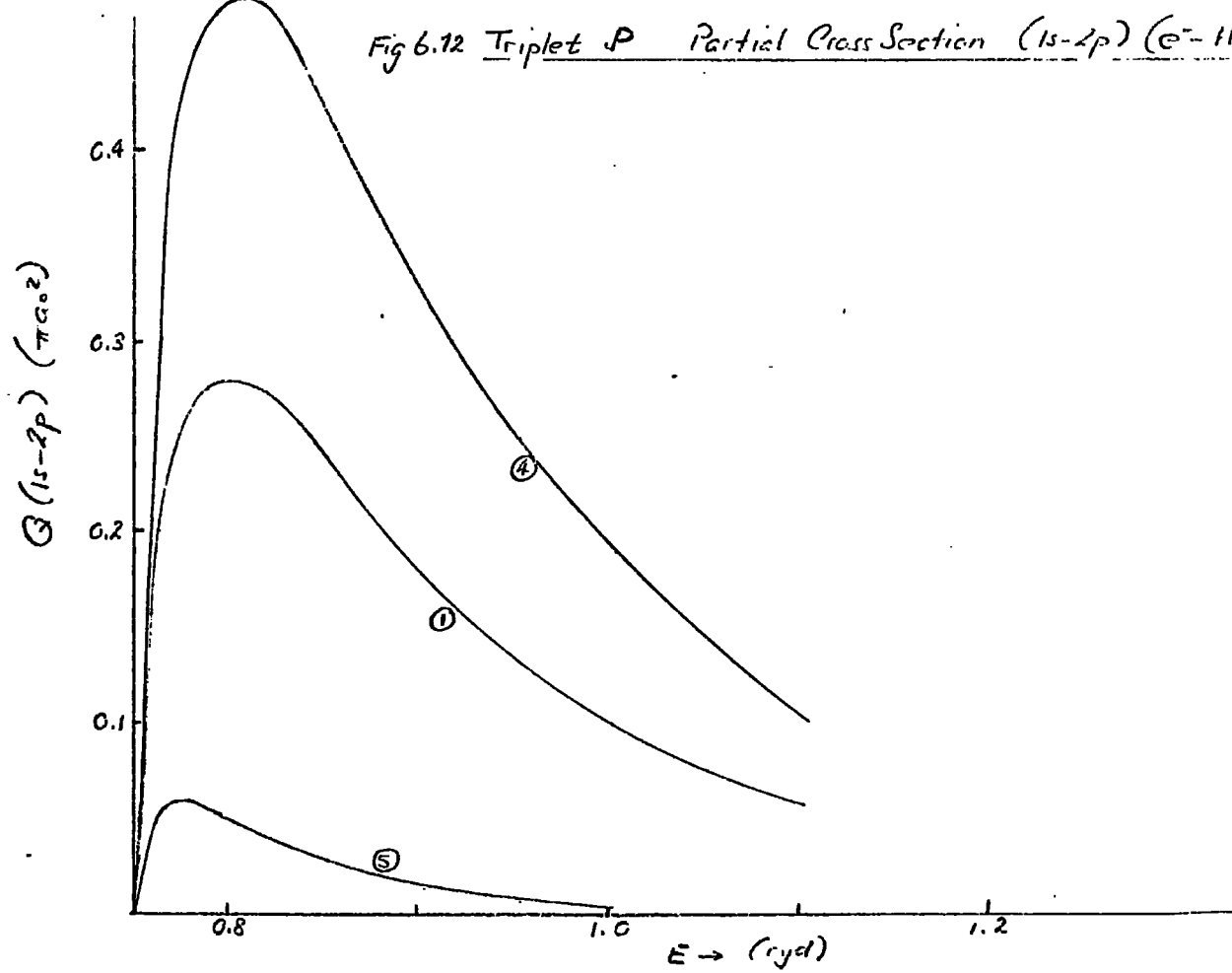
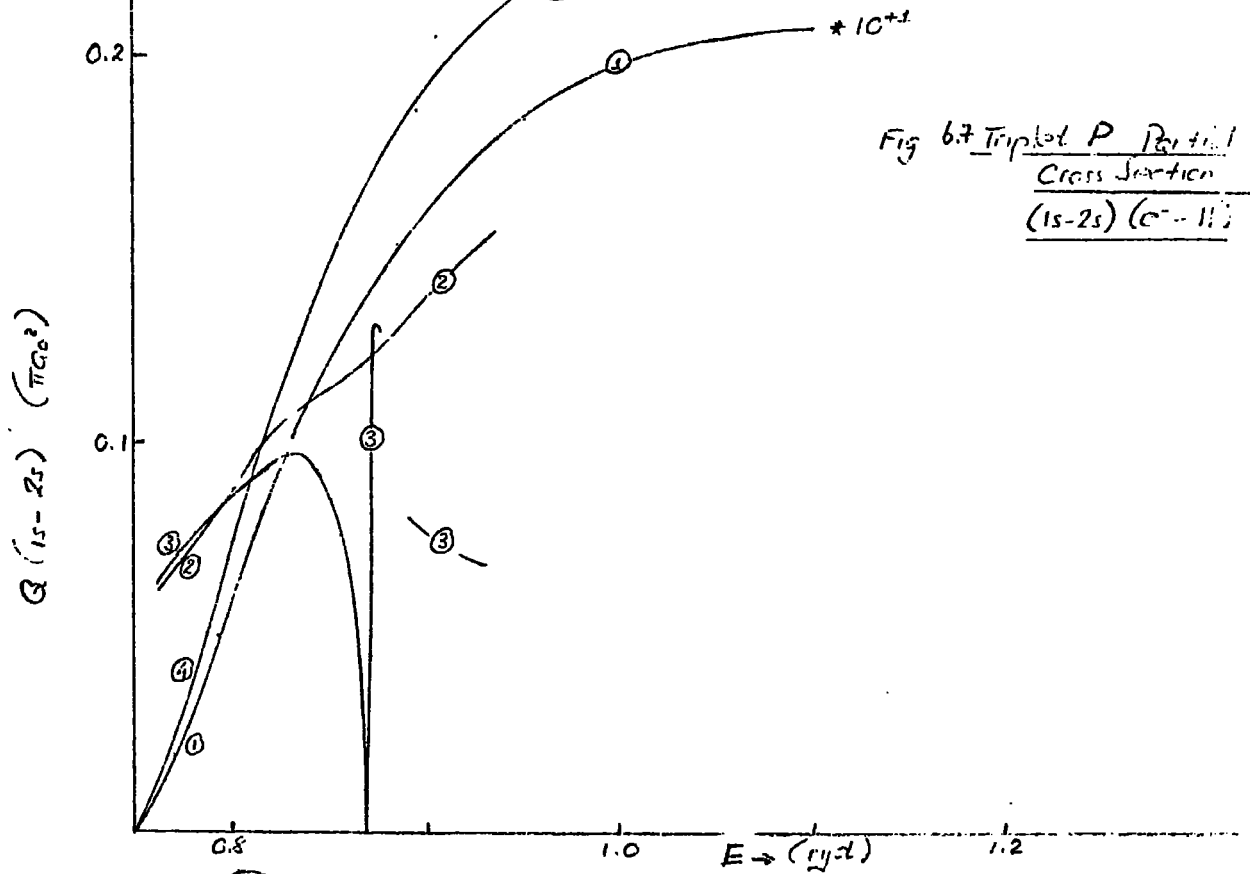


Fig 6.8

Singlet S Partial Cross Section  
(1s-2s) ( $e^- - H$ )

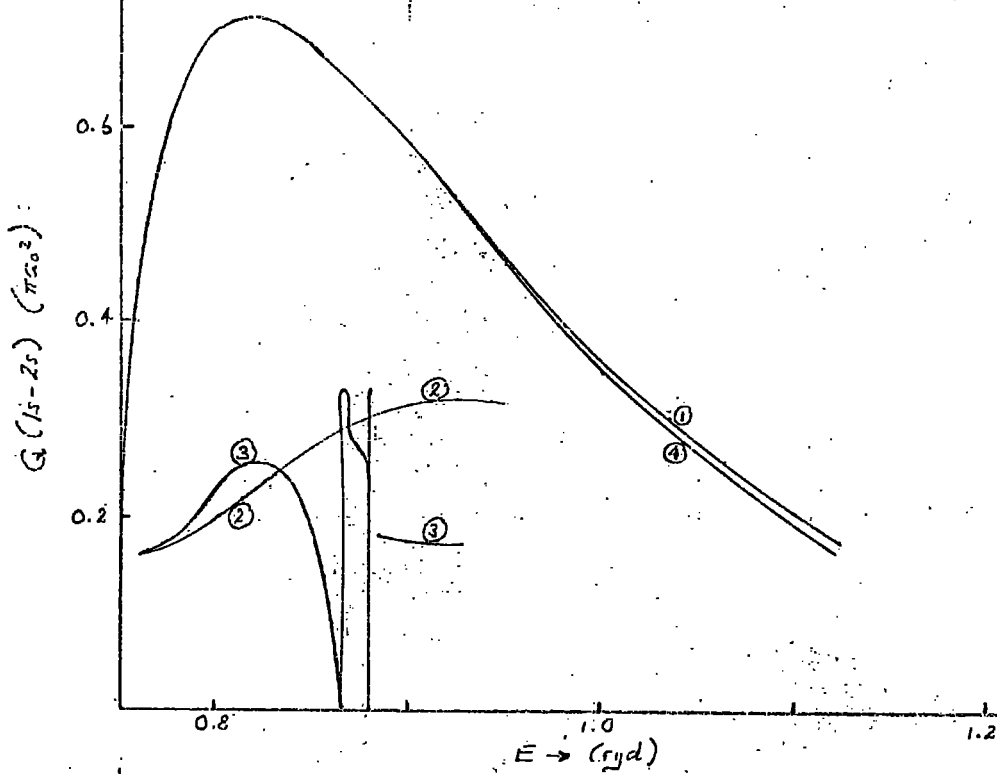


Fig 6.13 Singlet S Partial Cross Section  
(1s-2p) ( $e^- - H$ )

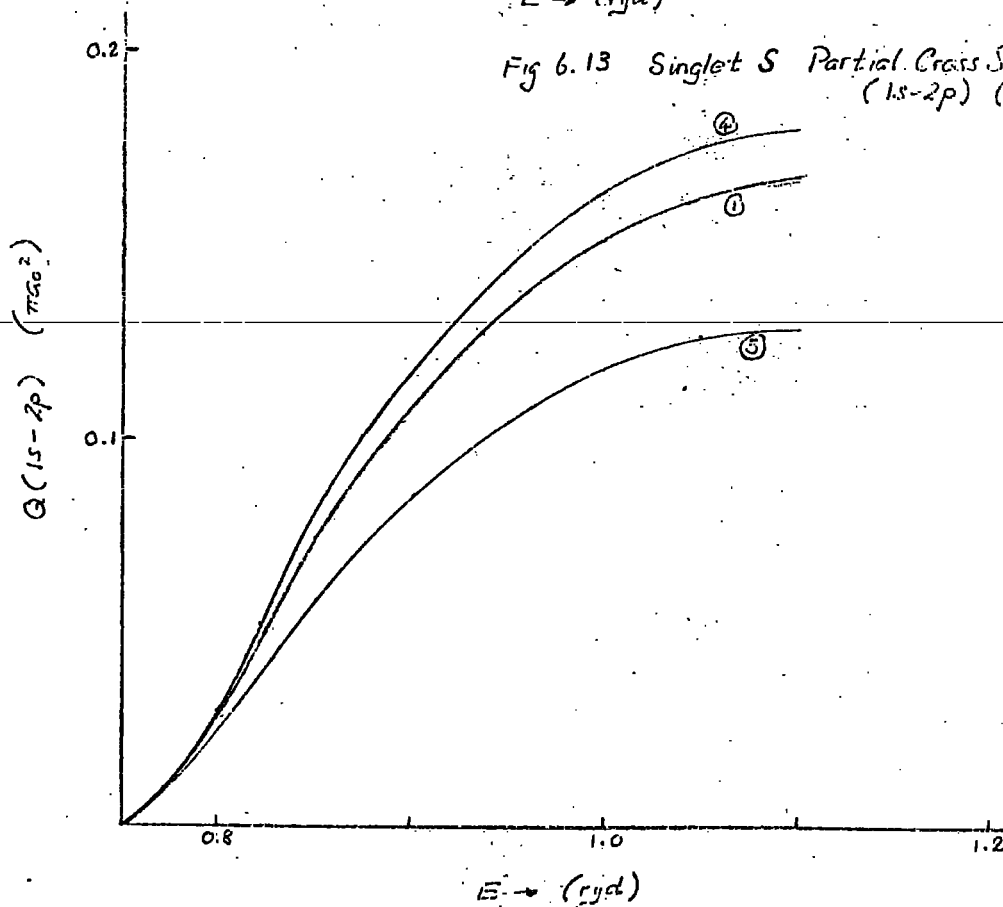


Fig 6.9 Singlet P Partial Cross Section  
(1s-2s) ( $e^- - H$ )

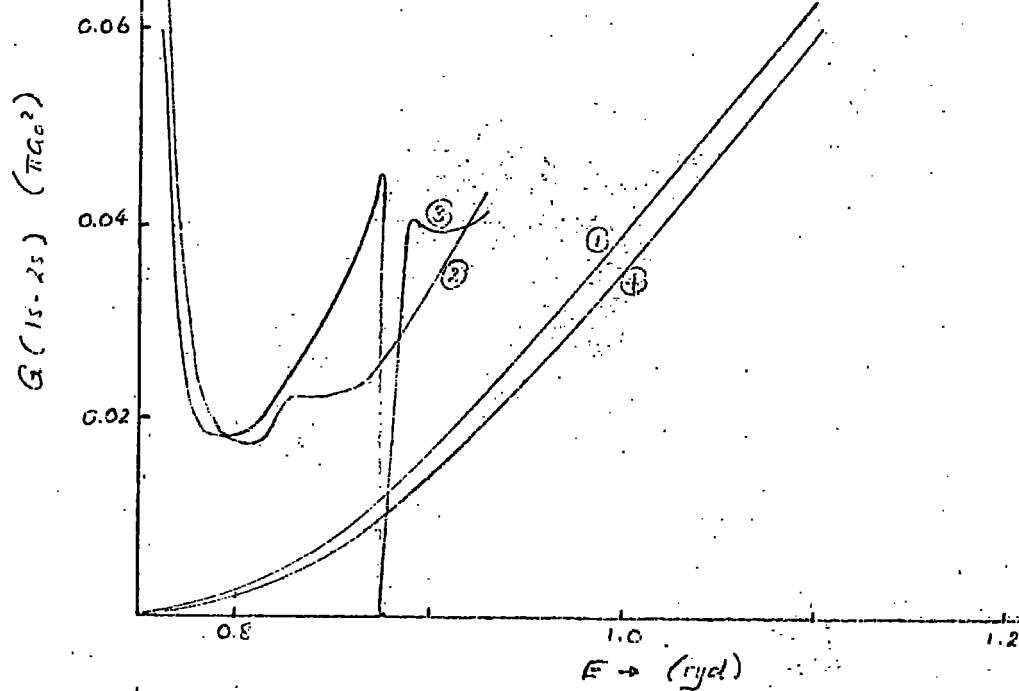


Fig 6.14 Singlet P Partial Cross Section  
(1s-2p) ( $e^- - H$ )

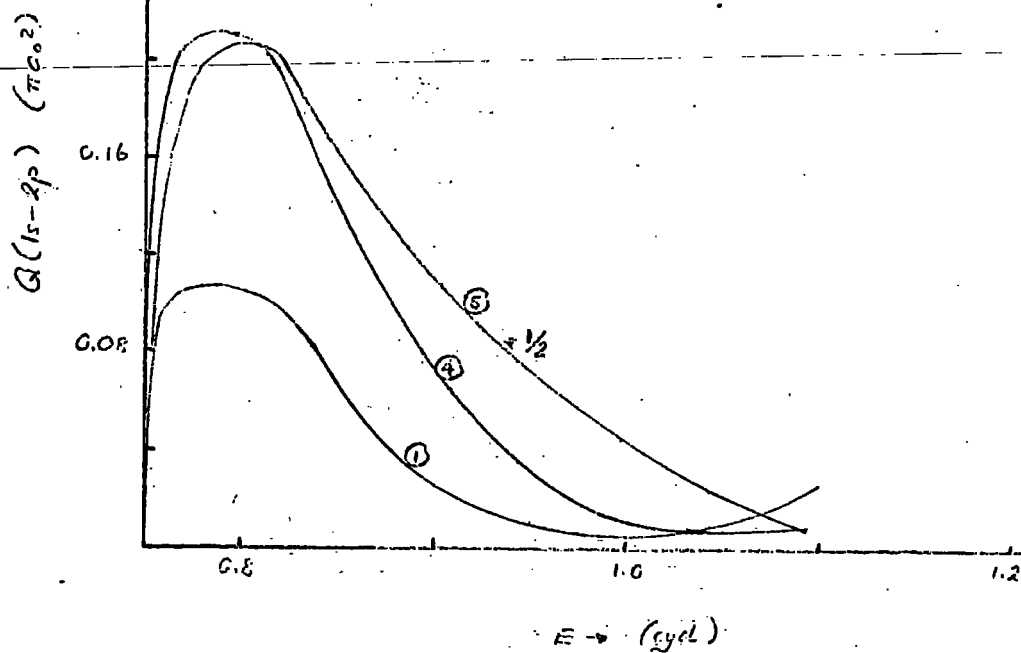


Fig 6.10 Singlet D Partial Cross Section  
(1s-2s) ( $e^- - H$ )

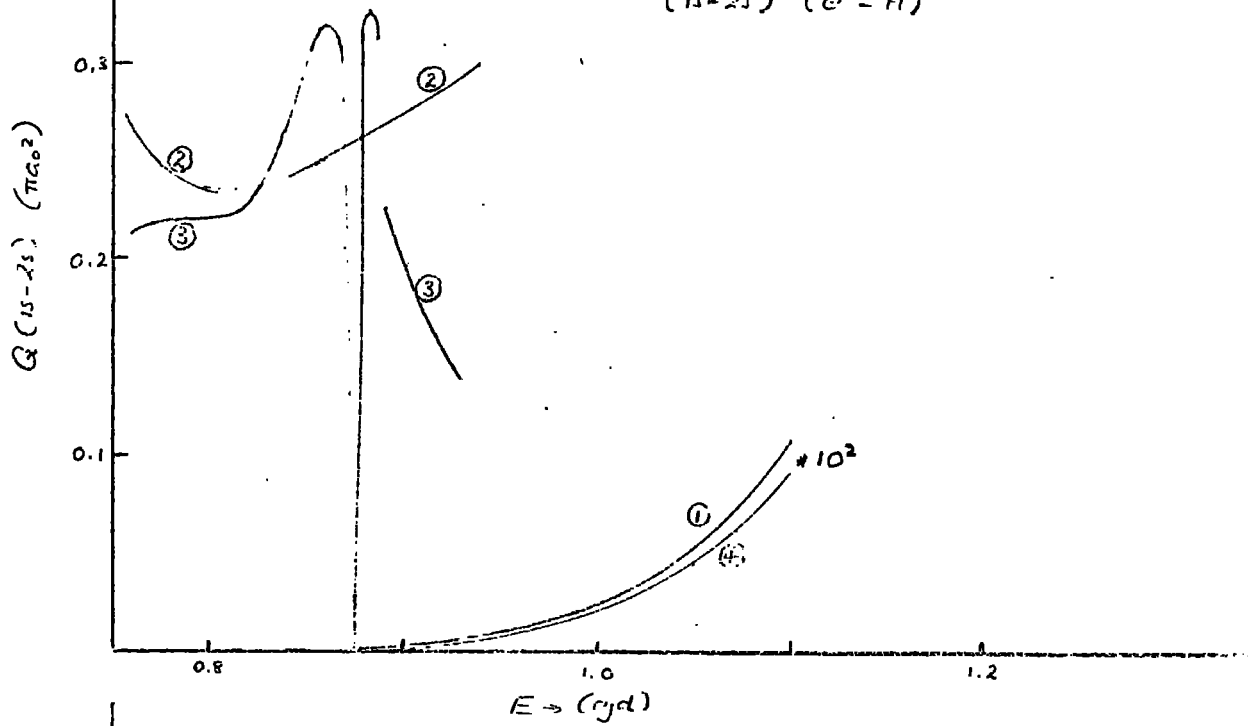
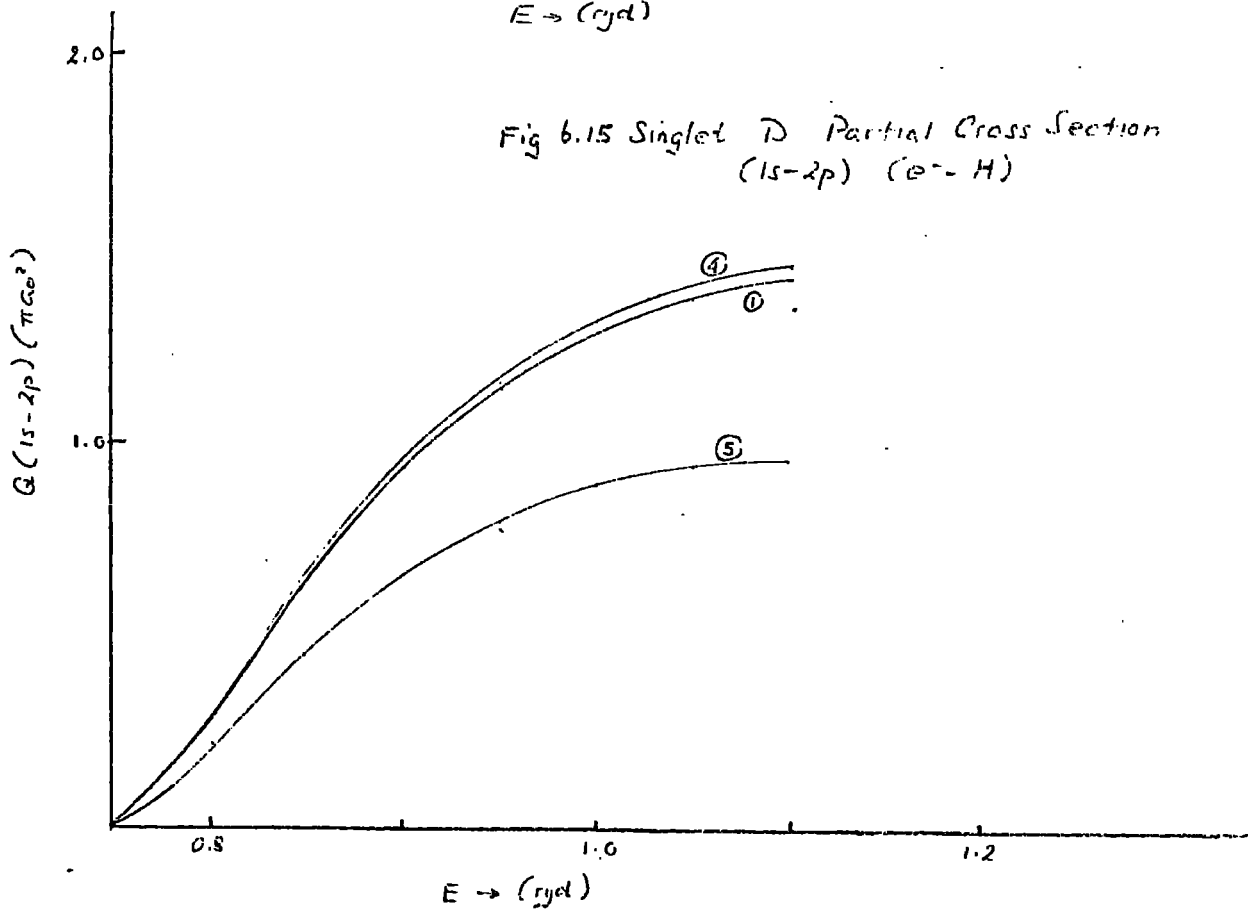


Fig 6.15 Singlet D Partial Cross Section  
(1s-2p) ( $e^- - H$ )





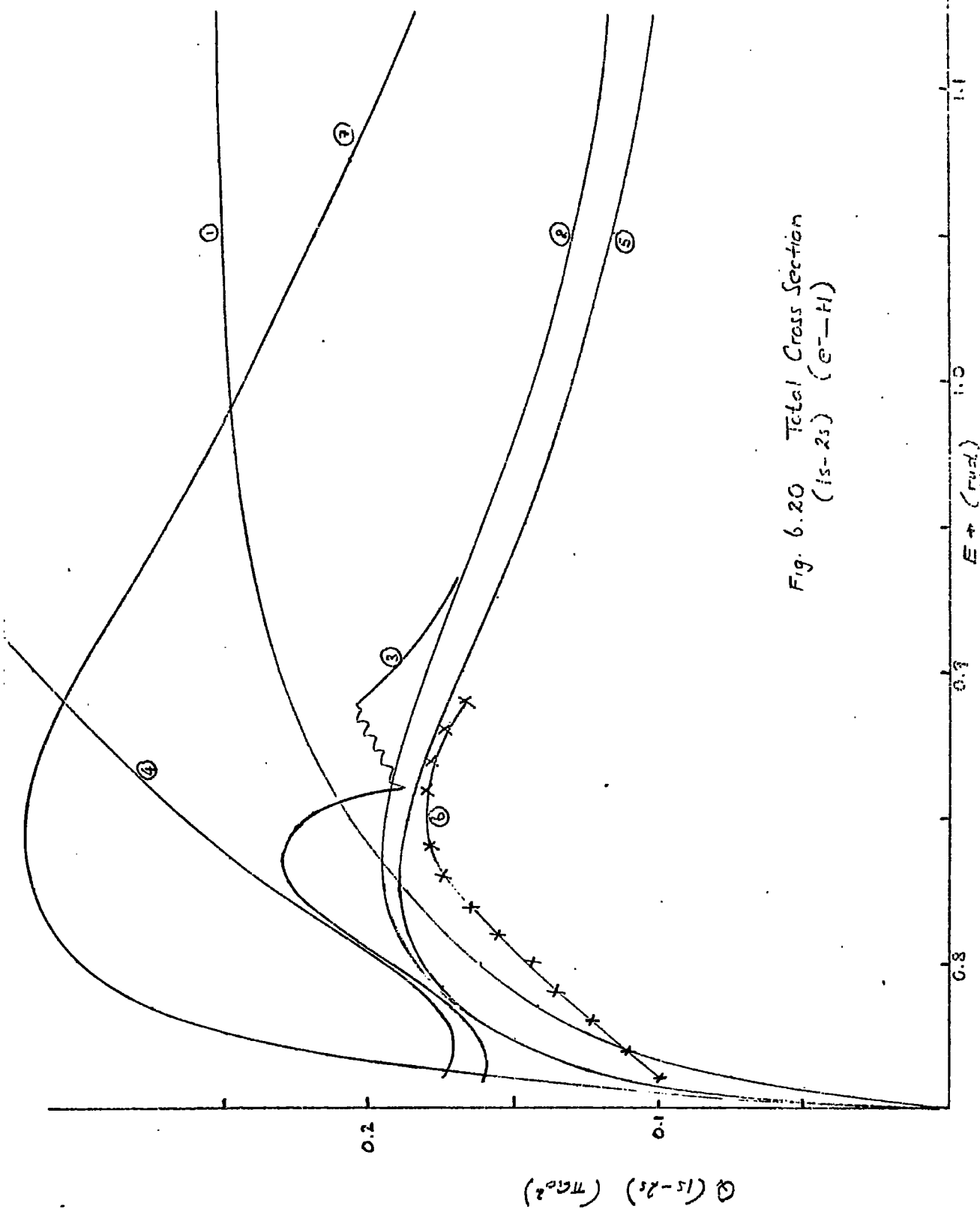


Fig. 6.20 Total Cross Section  
(1s-2s) ( $e^-$ -H)

Fig 6.21 Total Crass Section  $(15-2p)$  ( $\varepsilon-H$ )

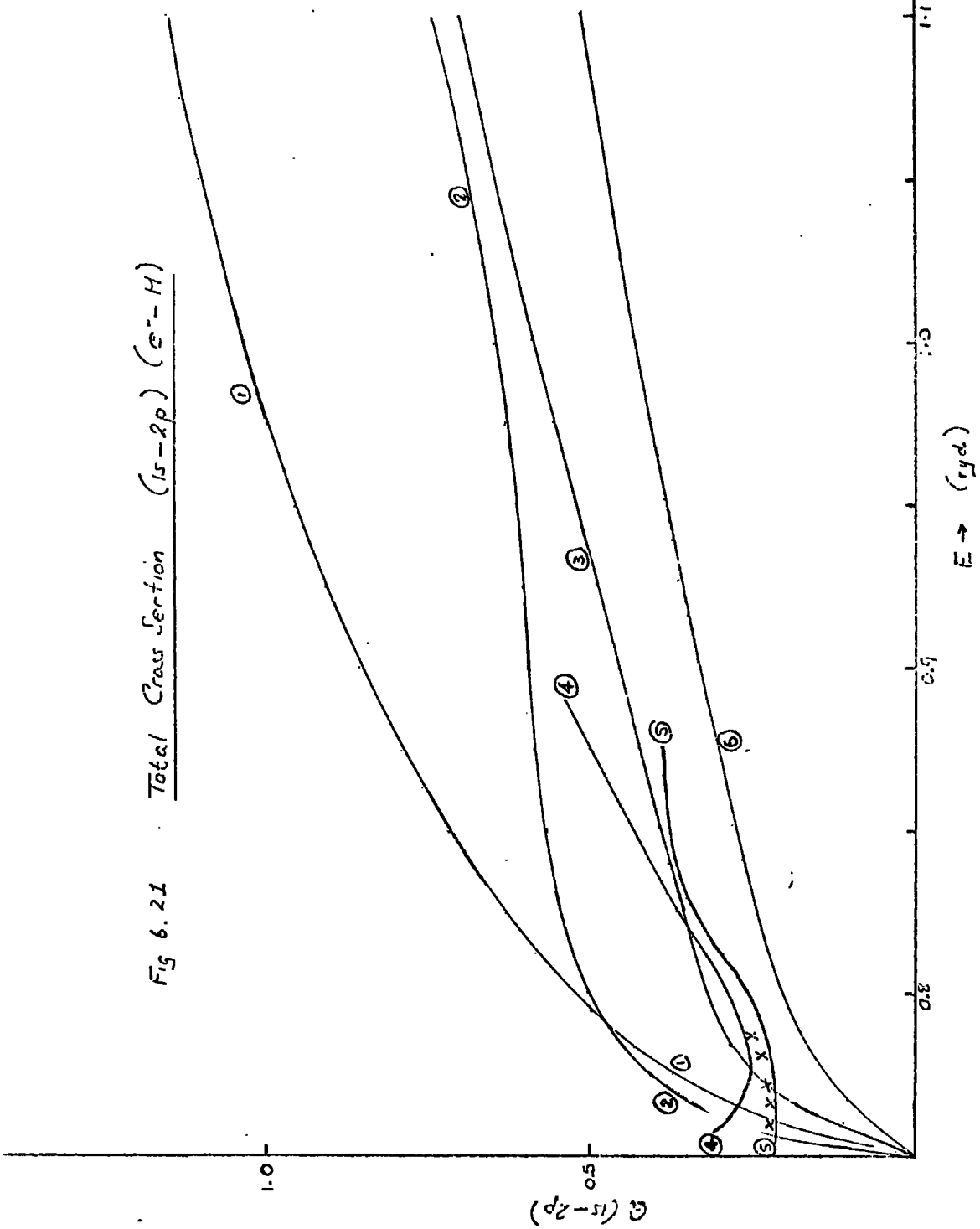


Fig 6.22 Total Crass Section (15-25) ( $e=H$ )

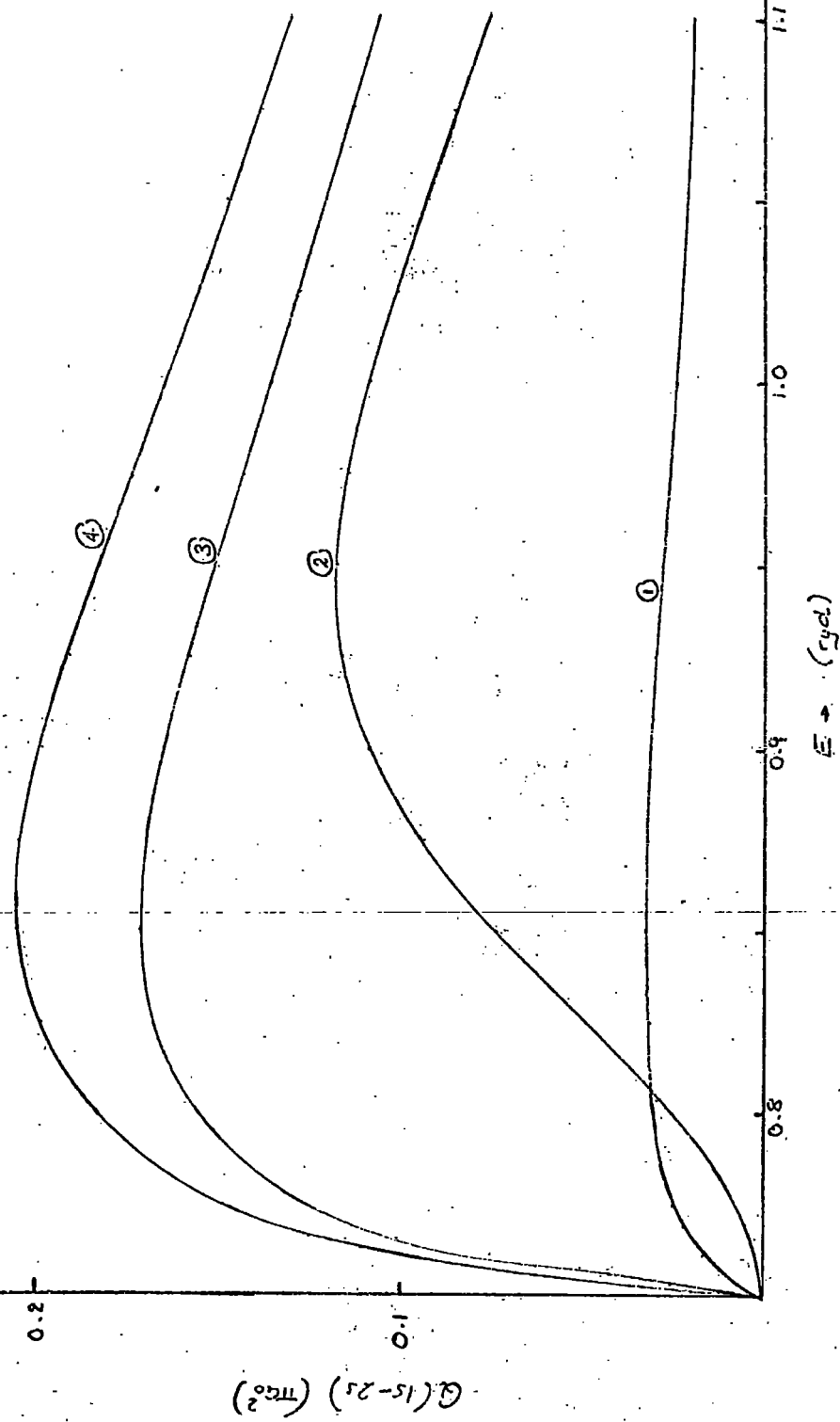


Fig 6.23

Total Cross Section (1s-2p) ( $e^-H$ )

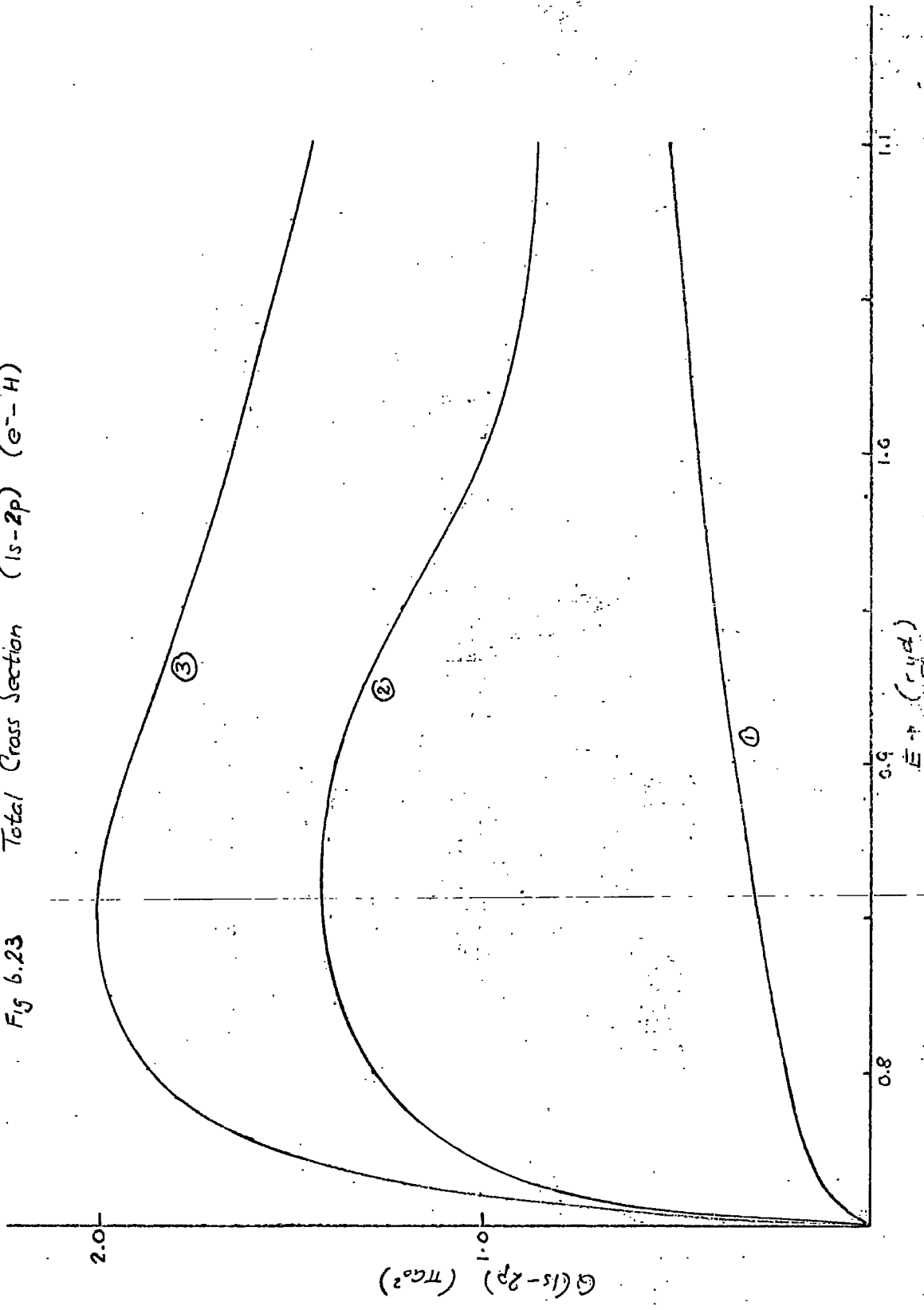


Fig 6.24 Total Cross Section (1s-2s) ( $e^- - H$ )

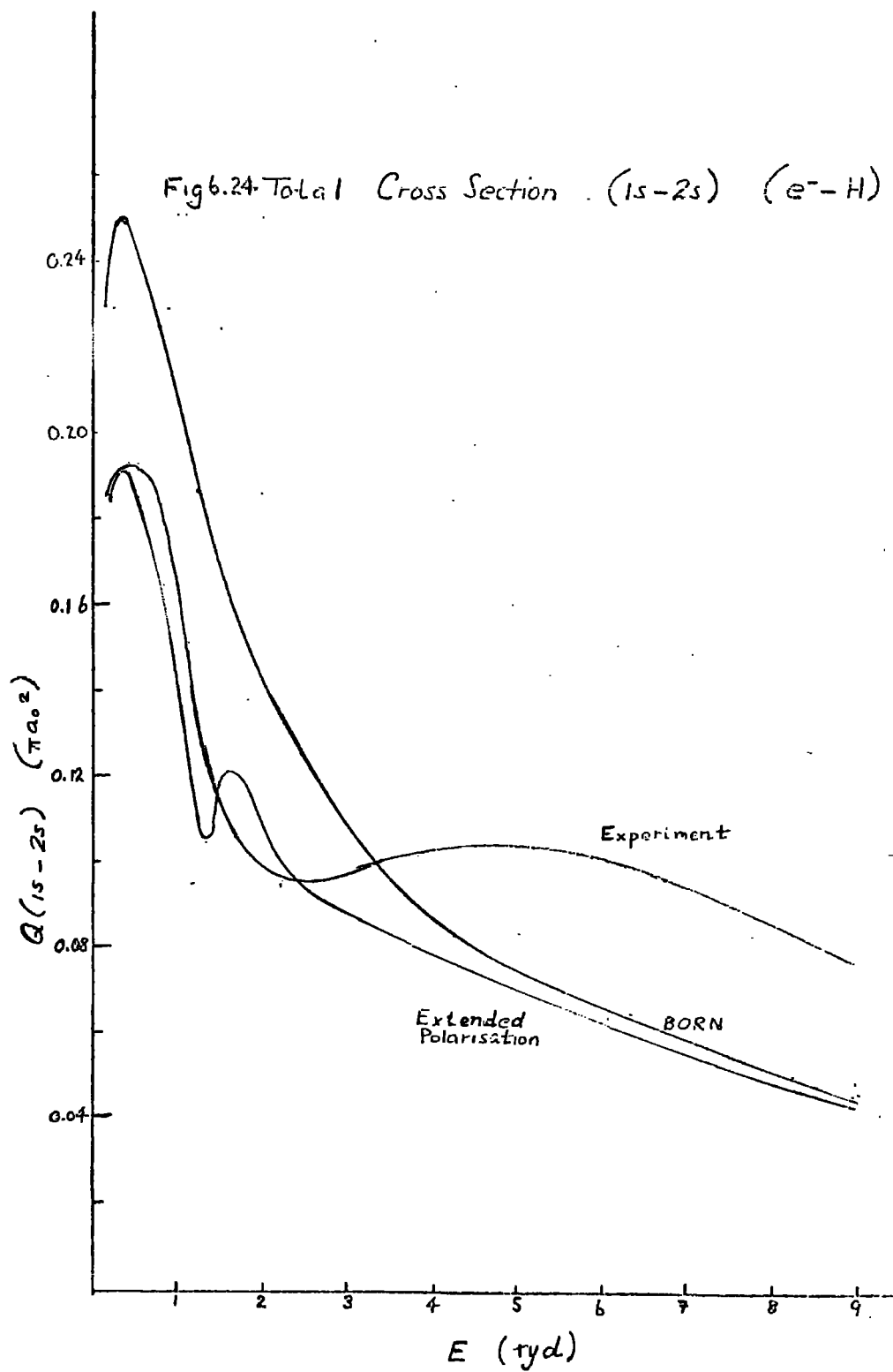
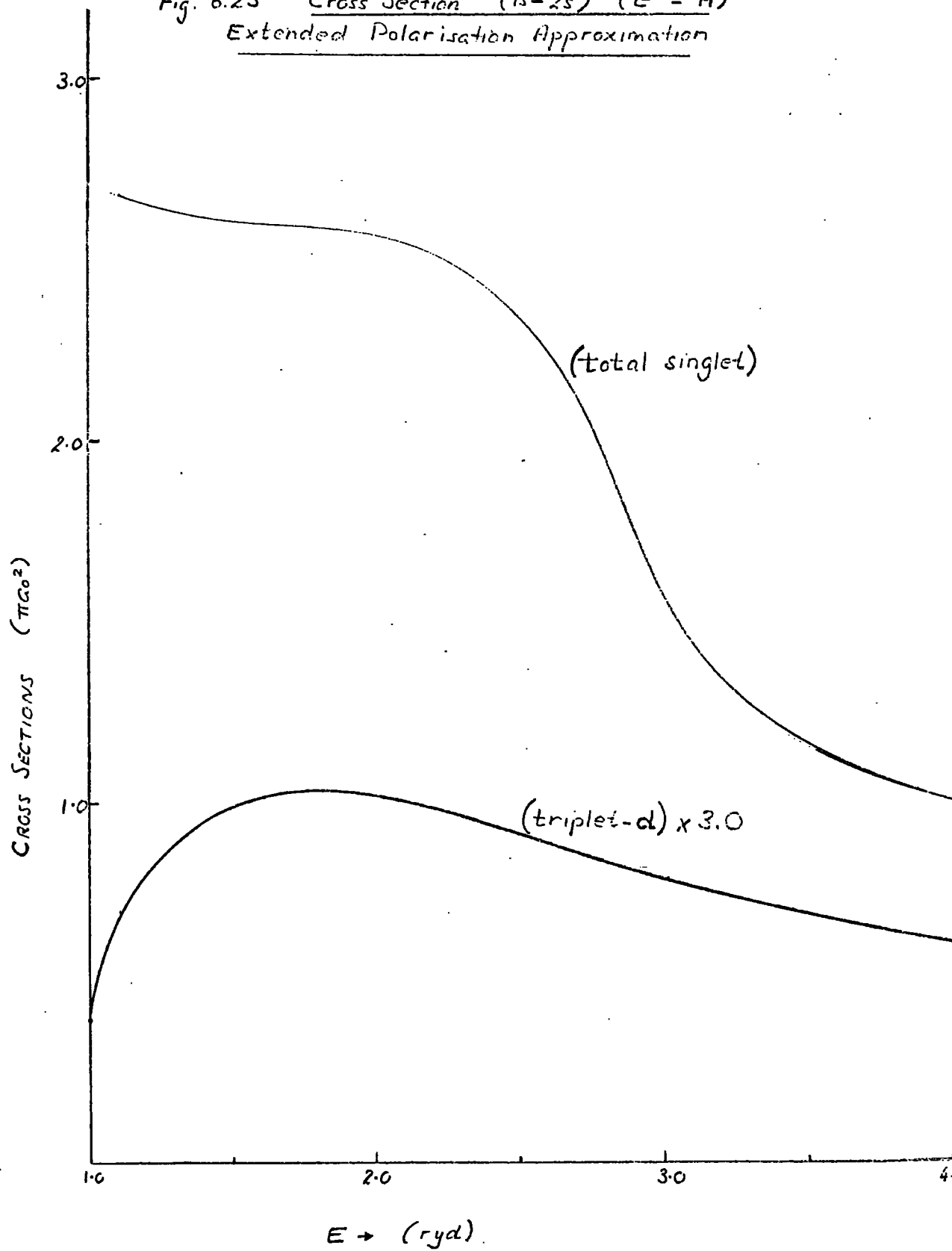


Fig. 6.25 Cross Section (1s-2s) ( $e^- - H$ )  
Extended Polarisation Approximation



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For the sake of brevity the above abbreviations are:-

P.P.S. = Proceedings of the Physical Society

P.R. = Physical Review.

P.R.S. = Proceedings of the Royal Society.

J.E.T.P. = Journal of Experimental and Theoretical Physics.

